

# Effects of speciation on partitioning of iodine in aqueous biphasic systems and onto ABEC<sup>®</sup> resins

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## Abstract

Polyethylene glycol (PEG)-aqueous biphasic systems (ABS) and PEG-grafted aqueous biphasic extraction chromatographic (ABEC) resins have been shown to remove inorganic species from environmental and nuclear wastes. The partitioning behavior of several iodide species (iodide, iodine, triiodide, iodate, and 4-iodo-2,6-dimethylphenol (I-DMP)) have been studied for PEG (MW 2000)-salt systems and ABEC resins. Iodide partitioning to PEG-rich phases or onto ABEC resins can be enhanced by derivatization with 2,6-dimethylphenol to form 4-iodo-2,6-dimethylphenol or by addition of I<sub>2</sub> to form triiodide. Conversely, iodide partitioning to the PEG-rich phase or onto ABEC resins is reduced by oxidation of iodide to IO<sub>3</sub><sup>-</sup>. Partitioning studies of iodide, iodate, and iodine in a PEG-ABS are compared to results using ABEC resins. © 2004 Elsevier B.V. All rights reserved.

**Keywords:** Partitioning; Aqueous two-phase systems; Iodide; Iodine; Iodate; Triiodide

## 1. Introduction

Aqueous biphasic systems (ABS) have been used as a gentle liquid/liquid separation methodology for large and small biomolecules [1], however, there is an increasing number of applications of ABS to liquid/liquid separation of inorganic ions and organic molecules [2–7]. Earlier results utilizing both polyethylene glycol (PEG)-ABS and the related aqueous biphasic chromatographic resin (ABEC) to separate and recover iodide from environmental and nuclear wastes [3] for either remediation or analysis, prompted this study to analyze the effects of iodine speciation on the liquid/liquid distribution values and compare them to ABEC batch uptakes. A simple separation and concentration procedure usable for all iodide species would be a valuable tool.

In solution, iodide can form many species and must be carefully examined in order to control the separation. It is known that in aqueous solutions, the following equilibria can exist [8]:



In neutral and acidic solutions these species are stable, but at high pH, iodine (as well as I<sub>3</sub><sup>-</sup> and I<sub>5</sub><sup>-</sup>) can disproportionate into iodide and IO<sub>x</sub><sup>-</sup> species [8]. One can predict from the small negative Gibbs free energy of hydration ( $\Delta G_{\text{hyd}}$ ), that the large, soft anions I<sub>3</sub><sup>-</sup> and I<sub>5</sub><sup>-</sup> would be chaotropic. On the other hand, IO<sub>x</sub><sup>-</sup> species having large negative  $\Delta G_{\text{hyd}}$  would be kosmotropic (water-structuring). The I<sup>-</sup> anion has a  $\Delta G_{\text{hyd}}$  that falls between those of the polyiodide anions and the oxo-iodide anions. Since phase preference for an inorganic solute in an ABS depends on its  $\Delta G_{\text{hyd}}$ , the partitioning of iodide in a PEG/salt ABS or onto ABEC will greatly depend on the speciation of iodide in solution.

Here, we present our investigation of the separation and quantification of iodide species from aqueous samples. Results from partitioning experiments in ABS systems and batch uptakes with ABEC resins for iodide, iodine, iodate, and the derivatized species, 4-iodo-2,6-dimethylphenol (I-DMP), are compared in order to validate the relationship between partitioning in a liquid/liquid ABS and uptake onto ABEC resins.

## 2. Experimental

### 2.1. Chemicals

The chemicals, NaI, NH<sub>4</sub>I, I<sub>2</sub>, PEG-2000, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, 2,6-dimethylphenol, 2-iodobenzoic acid, ascorbic

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dwcf the dry weight conversion factor relating the mass of the hydrated resin to its dry weight.

The ABEC resins contain a large amount of water (60–85 wt.%). This amount can vary depending upon temperature, humidity, and the treatment of the resins before use. Therefore, the ABEC resins were conditioned by washing with deionized water, then filtered on a 2 in. diameter Büchner funnel with a water aspirator (Whatman #2 qualitative filter disk), and then dried for 10 min by passing air first bubbled through a 500 ml Erlenmeyer flask containing 200 ml of deionized water through the resin bed. This ensures that the water content of the resins is constant from batch to batch.

The batch contacts were carried out following previously described methods [9]. The radiotracer was added to 2.2 ml of the solution of interest, mixed, and a 100 ml aliquot removed for analysis ( $A_i$ ). One milliliter of the spiked solution (contact volume) was added to two separate samples of conditioned ABEC resin of known mass (typically 15–30 mg). The contacted samples are centrifuged for 2 min and then gently stirred for 30 min, followed by another 2 min of centrifugation (to ensure the resin remained in contact with the solution). The solution was stirred for another 30 min after which the solution was filtered through a 0.45  $\mu\text{m}$  pipette-tip filter. A 100  $\mu\text{l}$  aliquot was then removed for radioanalysis ( $A_f$ ). The distribution ratios ( $D$  and  $D_w$ ) reported here are the average of at least two measurements and are typically accurate to  $\pm 5\%$ .

### 3. Results and discussion

#### 3.1. Liquid/liquid iodide species partitioning studies

The salting-out abilities of inorganic salts on PEG to form ABS can be related to the  $\Delta G_{\text{hyd}}$  of the salt's anion [10]. Anions of water structuring, kosmotropic, salts that strongly interact with water (i.e., have large  $-\Delta G_{\text{hyd}}$ ) such as  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ , and even  $\text{OH}^-$ , will salt-out PEG-2000 to form a biphasic system. Table 1 provides the  $\Delta G_{\text{hyd}}$  for several anions for comparison. On a molar basis, the more neg-

Table 1  
Gibbs free energy of hydration for selected anions

Ion	$\Delta G_{\text{hyd}}$ (kJ/mol) <sup>a</sup>
$\text{TcO}_4^-$	-251
$\text{ReO}_4^-$	-234
$\text{I}_3^-$	11
$\text{I}^-$	-283
$\text{IO}_3^-$	-408
$\text{HCO}_3^-$	-368
$\text{OH}^-$	-439
$\text{SO}_4^{2-}$	-1090
$\text{CO}_3^{2-}$	-1315
$\text{PO}_4^{3-}$	-2773

<sup>a</sup> Data from [13,14].

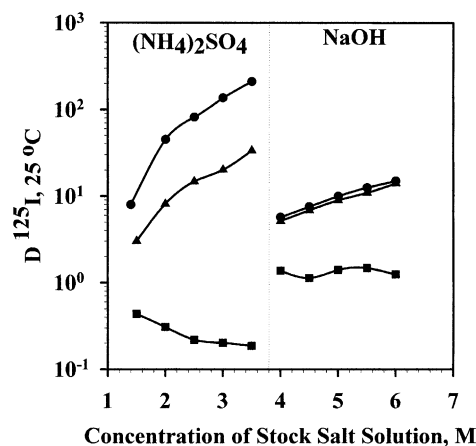


Fig. 1. Distribution for  $^{125}\text{I}^-$  ( $\blacktriangle$ ),  $^{125}\text{IO}_3^-$  ( $\blacksquare$ ), and  $^{125}\text{I}$ -2,6-DMP ( $\bullet$ ) in 40% PEG-2000/ $(\text{NH}_4)_2\text{SO}_4$  and 40% PEG-2000/NaOH ABS.

ative the anion's  $\Delta G_{\text{hyd}}$ , the less salt is required to salt-out a given amount of PEG. A similar but smaller effect can be attributed to the cation, however, here we will focus on anionic species.

Phase diagrams of PEG-2000/salt ABS reveal that as the concentration of polymer and/or salt increase (or if there is an increase in temperature) the phases become increasingly divergent. That is, if you increase the system components, the PEG-rich phase excludes more salt and the salt-rich phase excludes more PEG [11,12].

While salts with kosmotropic anions salt-out PEG-2000 to form an ABS, water destructuring, chaotropic, anions with small  $|\Delta G_{\text{hyd}}|$  partition to the PEG-rich phase of such an ABS. We have previously demonstrated this feature with quantitative partitioning of  $^{99}\text{TcO}_4^-$  to the PEG-rich phase of several high ionic strength solutions [3]; a property which we have exploited in the removal of  $^{99}\text{TcO}_4^-$  from simulants of the highly alkaline radioactive waste tanks at the Hanford, WA site [4] and from solutions of  $\text{MoO}_4^{2-}$  in caustic found in  $^{99\text{m}}\text{Tc}$ -generator technologies [15]. In addition, the similarities between  $\text{TcO}_4^-$  and  $\text{ReO}_4^-$ , has allowed development of effective separations strategies for  $\text{ReO}_4^-/\text{WO}_4^{2-}$  and  $\text{ReO}_4^-/\text{MoO}_4^{2-}$  [16], important separations in radiopharmacy and hydrometallurgy.

Based on the  $\Delta G_{\text{hyd}}$  for  $\text{I}^-$  (Table 1), this ion should partition to the PEG-rich phase of a PEG/salt ABS, and indeed, this has been demonstrated [17]. It became evident however, that the effect of speciation of iodine must be carefully examined [18] in order to control the separation. Fig. 1 plots the distribution ratios for three different iodine species in PEG-2000/ $(\text{NH}_4)_2\text{SO}_4$  and PEG-2000/NaOH ABS. Iodate has the lowest distribution ratios (actually preferring the lower salt-rich phase) which corresponds to its larger  $|\Delta G_{\text{hyd}}|$ , whereas, iodide with the smaller  $|\Delta G_{\text{hyd}}|$  has larger  $D$  values, preferring the upper PEG-rich phase.

Small aromatic molecules (e.g., benzene and substituted benzenes) have been shown in our laboratory to partition to the PEG-rich phase in several ABS [6,7]. These

small-uncharged molecules partition quantitatively to the PEG-rich phase in many of these systems and the preference for the PEG-rich phase tends to increase with the hydrophobicity of the aromatic solute. In an effort to increase the partitioning of iodide to the PEG-rich phase, experiments were conducted to utilize this preference of small, uncharged aromatic molecules for the PEG-rich phase to enhance  $I^-$  partitioning by derivatizing iodide to 4-iodo-2,6-dimethylphenol species (I-DMP). We predicted an increase in the distribution ratios of iodide upon conversion of the free ion to a covalently bound aromatic species. This was in fact observed as shown by the distribution ratios for I-DMP plotted in Fig. 1.

Trends normally apparent in distribution ratios of solutes in PEG/salt ABS as a function of salt concentration are readily seen in Fig. 1. As the concentration of salt increases, the difference in PEG and salt concentrations in each phase increases. This increase in phase divergence results in an increased affinity of a solute for its preferred phase [11,12,19]. Thus, the distribution ratios for  $I^-$  and I-DMP (which prefer the PEG-rich phase) increase, while the distribution ratios for  $IO_3^-$  (which prefers the salt-rich phase) decrease.

Since the derivatization reaction is best carried out in a slightly basic solution due to the solubility of the derivatizing reagents [8], the distribution ratios of the same three iodine species presented above were also examined from NaOH ABS (Fig. 1). While the distribution values of iodate and iodide mimic the ammonium sulfate system, (when the lower salting-out ability of NaOH is considered) it is not readily apparent why the distribution ratios for I-DMP are not significantly improved over those of iodide in NaOH. We suspect, however, this may be due to hydroxide substitution of the iodide on the I-DMP reforming free iodide, indeed the measured distribution values from NaOH are almost identical to free iodide.

### 3.2. Effect of pH on iodide species partitioning

The results obtained from the previous experiment led to the exploration of the effect of pH on the partitioning behavior of iodide, iodate, and I-DMP. Fig. 2 (filled symbols) plots the distribution of the three iodine species in a PEG-2000/2.5 M  $(NH_4)_2SO_4$  ABS where the pH of the salt solution was modified by adding small aliquots of sulfuric acid or sodium hydroxide. One observes relatively small changes in the partitioning of the three iodine species as the pH is increased.

Covalent attachment of PEG to a polystyrene/divinylbenzene resin bead (the ABEC resins) allows us to carry out similar separations in a batch mode. The conditions which allow or improve separations in liquid/liquid ABS also cause retention on the analogous ABEC resins [5,20,21]. The same experiment described above was conducted using the ABEC-5000 resin (Fig. 2, open symbols). There is an observable decrease in  $D_W$  for the iodide and I-DMP on the ABEC resin as the pH of the salt solution is increased. This

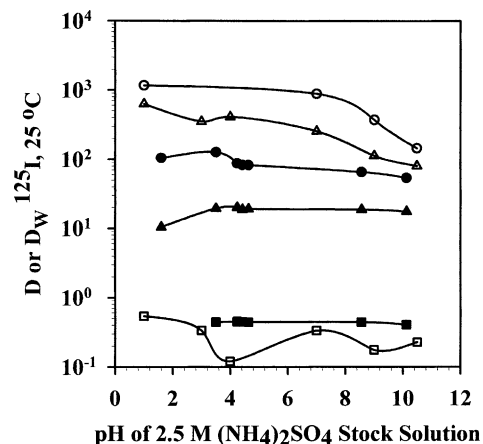


Fig. 2. Distribution for  $^{125}I^-$  ( $\blacktriangle$ ),  $^{125}IO_3^-$  ( $\blacksquare$ ), and  $^{125}I$ -2,6-DMP ( $\bullet$ ) in 40% PEG-2000/2.5 M  $(NH_4)_2SO_4$  ABS (filled symbols) and ABEC-5000 (open symbols) vs. pH.

may be due to the longer contact times in the batch  $D_W$  experiment allowing for hydroxide substitution on the I-DMP, thus lowering the distribution ratios at high pH. Notice that changing the pH of a 2.5 M  $(NH_4)_2SO_4$  solution has little effect on the relative distribution ratios for the iodate species.

### 3.3. Effect of added iodine on iodide partitioning in ABS and onto ABEC

We have also studied the effect of the addition of  $I_2$  as a complexant. Addition of iodine enhances the formation of triiodide, which will partition more favorably to the PEG-rich phase or onto ABEC resins based on its  $\Delta G_{hyd}$  (Table 1). Fig. 3 shows that even small amounts of iodine can improve the distribution of iodide to the ABEC resin in 3.5 M  $(NH_4)_2SO_4$ . Fig. 3 also illustrates the effect of the molecular weight of the polymer attached to the solid support in the ABEC resins. The higher the molecular weight of the polymer, the higher the distribution to the ABEC resin,

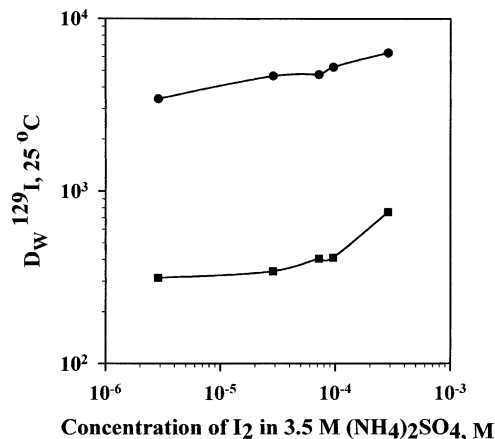


Fig. 3.  $D_W$  for  $^{129}I^-$  in 3.5 M  $(NH_4)_2SO_4$  vs. concentration of added  $I_2$ : ABEC-5000 ( $\bullet$ ), ABEC-2000 ( $\blacksquare$ ).

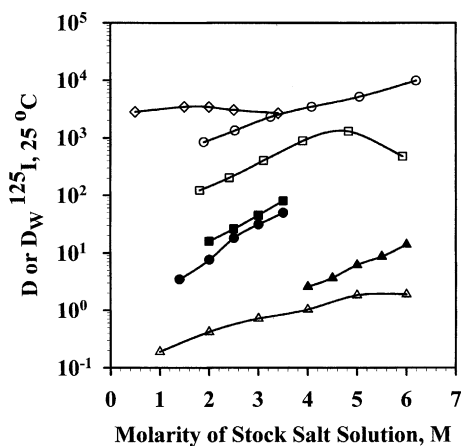


Fig. 4. Distribution of  $^{125}\text{I}^-$  vs. concentration of stock salt solution onto ABEC-5000 ( $D_W$ : open symbols) and in 40% PEG-2000/salt ABS ( $D$ : filled symbols) from  $\text{KHCO}_3$  ( $\blacklozenge$ ),  $(\text{NH}_4)_2\text{SO}_4$  ( $\bullet$ ),  $\text{K}_2\text{CO}_3$  ( $\blacksquare$ ), or  $\text{NaOH}$  ( $\blacktriangle$ ).

although studies are currently underway to quantify the PEG coverage on each resin bead.

### 3.4. Iodide partitioning in ABS and onto ABEC from different salt solutions

To further characterize the uptake of iodine species in ABS and to ABEC resins, the partitioning behavior of iodide in several salt ABS was investigated. Fig. 4 plots  $D$  and  $D_W$  values for iodide versus increasing concentration of  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{KHCO}_3$  (ABEC only), and  $\text{NaOH}$  in PEG-2000 ABS, and onto ABEC-5000. It is interesting to note that the trend for distribution ratios for a chaotropic anion such as pertechnetate increases with increasing  $|\Delta G_{\text{hyd}}|$  of the salting-out agent, [15,20] does not seem to hold true for iodide with the ABEC resin, i.e., iodide has a lower  $D_W$  value in the  $\text{K}_2\text{CO}_3$  salt system, than in the  $(\text{NH}_4)_2\text{SO}_4$  system. However, as discussed earlier (Fig. 2), increasing pH has an adverse effect on  $D_W$ . The pH of the  $\text{K}_2\text{CO}_3$  system is above 10 and at a pH above 9, the equilibrium favors the formation of hypoiodate from triiodide,  $\text{I}_3^-$ , in the presence of base [22]. The discrepancy between ABS and ABEC (in this example) is most likely due to the kinetics of formation of hypoiodate species. In the ABS experiment, the two phases are in contact with each other for only ca. 4 min and only a small portion of the  $\text{I}^-$  present will have time to react in the highly alkaline  $\text{K}_2\text{CO}_3$  solution. In the ABEC experiment, the  $\text{I}^-$  is in contact with the  $\text{K}_2\text{CO}_3$  solution for at least 60 min allowing for the formation of more hypoiodate species, thus lowering the distribution onto the resin. It is suggested that standardized solutions of triiodide be maintained between pH 7–9 to minimize the disproportionation reaction [23].

In an effort to try to further understand this partitioning data, the uptakes of the pertechnetate probe onto ABEC-5000 from  $\text{KHCO}_3$  were measured (data not shown).

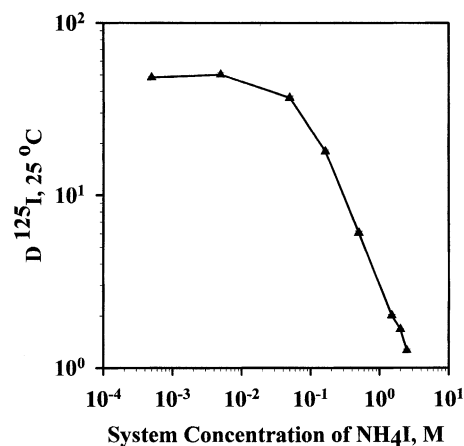


Fig. 5. Distribution ratios  $\text{I}^-$  in 40% PEG-2000/3.5 M  $(\text{NH}_4)_2\text{SO}_4$  ABS vs. the system concentration of  $\text{NH}_4\text{I}$ .

Partitioning for pertechnetate follows the expected trend based on  $|\Delta G_{\text{hyd}}|$  (i.e.,  $D_{\text{TcO}_4^-}$  decreases in the order  $\text{K}_2\text{CO}_3 > (\text{NH}_4)_2\text{SO}_4 > \text{NaOH} > \text{KHCO}_3$ ) [15,20,24]. Based on the disproportionation reaction discussed above, iodide should partition better in  $\text{KHCO}_3$  than in  $\text{K}_2\text{CO}_3$  because the  $\text{K}_2\text{CO}_3$  solution pH is higher and will promote the formation of hypoiodate. Fig. 4 shows the uptake of iodide onto ABEC-5000 from  $\text{K}_2\text{CO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NaOH}$ , and  $\text{KHCO}_3$ , and indeed partitioning for  $\text{I}^-$  is better in the  $\text{HCO}_3^-$  system than the  $\text{CO}_3^{2-}$  system. Also note that in the  $\text{NaOH}$  system which is the most alkaline, the partitioning of  $\text{I}^-$  is the poorest.

### 3.5. Capacity of a PEG/salt ABS for iodide

Finally, in order to understand the capacity of the ABS, the partitioning behavior for  $\text{I}^-$  as the concentration of  $\text{NH}_4\text{I}$  is increased was examined (Fig. 5). There is a noticeable decline in  $D_I$  as  $\text{I}^-$  concentration increases above 0.05 M  $\text{NH}_4\text{I}$ . This would indicate that the amount of  $\text{NH}_4\text{I}$  in the PEG-rich phase of a PEG-2000/3.5 M  $(\text{NH}_4)_2\text{SO}_4$  ABS is approaching its solubility limit. It is interesting to note that at a system concentration of 0.5 M  $\text{NH}_4\text{I}$ , the ABS is inverted, that is the PEG-rich phase is now the more-dense bottom phase and the salt-rich phase is the less-dense upper phase.

## 4. Conclusions

Several key aspects of iodide partitioning in ABS and adsorption onto ABEC resins have been explored in this study. Iodide partitions to the PEG-rich phase of a PEG-2000/salt ABS and onto ABEC-5000 and ABEC-2000 resins, while iodate does not. Iodide can be separated from  $\text{IO}_3^-$  using these methods. The partitioning of iodide can also be enhanced by derivatization with 2,6-dimethylphenol to 4-iodo-2,6-dimethylphenol or complexation with  $\text{I}_2$ , increasing its preference for the PEG-rich phase of an ABS

or to ABEC resins by an order of magnitude. However, the derivatization must take place prior to addition to the high salt solutions used in ABS and ABEC procedures.

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