Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

The Effects of Halide Anions on the Partitioning Behavior of Pertechnetate in Polyethylene Glycolbased Aqueous Biphasic Systems

Robin D. Rogers[a]; Jianhua Zhang[a]; Scott T. Griffin[a]
[a] Department of Chemistry, Northern Illinois University, DeKalb, IL

To cite this Article Rogers, Robin D. , Zhang, Jianhua and Griffin, Scott T.(1997) 'The Effects of Halide Anions on the Partitioning Behavior of Pertechnetate in Polyethylene Glycolbased Aqueous Biphasic Systems', Separation Science and Technology, 32: 1, 699 — 707

To link to this Article: DOI: 10.1080/01496399708003224

URL: http://dx.doi.org/10.1080/01496399708003224

SEPARATION SCIENCE AND TECHNOLOGY, 32(1-4), pp. 699-707, 1997

THE EFFECTS OF HALIDE ANIONS ON THE PARTITIONING BEHAVIOR OF PERTECHNETATE IN POLYETHYLENE GLYCOL-BASED AQUEOUS BIPHASIC SYSTEMS

Robin D. Rogers,* Jianhua Zhang, and Scott T. Griffin
Department of Chemistry, Northern Illinois University, DeKalb, IL 60115

ABSTRACT

The pertechnetate anion quantitatively partitions to the upper polyethylene glycol (PEG)-rich phase in aqueous biphasic systems (ABS) formed by the addition of aqueous high-molecular-weight PEG solutions to aqueous water-structuring salt solutions. Most metal cations partition to the salt-rich phase in these systems. Other matrix ions, such as those that might be present in real-world waste streams, affect the distribution ratios observed for TcO_4^-, however, the effects are not well understood. The halide ions F^-, Cl^-, Br^-, I^- represent a wide range of water-structuring to chaotropic ions. The heavier halide ions have distribution ratios above one and are observed to follow the order $D_I > D_{Br} > D_{Cl}$. These ions depress D_{Tc}. Fluoride salts-out PEG and thus partitions primarily to the salt-rich phase and fluoride increases D_{Tc}. These trends can be correlated with the ions' Gibbs free energies of hydration (ΔG_{hyd}), a measure of their interactions with water. Based upon these results, it is possible to predict which ions will depress, elevate, or not affect D_{Tc} for a given PEG-ABS based upon the matrix ion's ΔG_{hyd}.

INTRODUCTION

Aqueous biphasic systems (ABS) are formed when polyethylene glycol (PEG) is salted out by certain water-structuring inorganic anions (e.g., OH^-, SO_4^{2-}, CO_3^{2-}, PO_4^{3-}) (1-5). The upper phase is PEG-rich and the lower phase is salt-rich; however, both phases are over 80% water and are suitable for liquid/liquid extraction. PEG-based ABS have key advantages over oil/water solvent extraction technologies. The PEGs are inexpensive, non-toxic (some are even FDA approved for internal consumption), non-flammable, and commercially available. The salts can be chosen from a variety of inexpensive, relatively harmless possibilities. Toxic, volatile organic diluents are not required, and thus secondary wastes are much less hazardous and disposal is easier. PEG-ABS can also operate over a wide range of temperatures and pH and thus have the potential to be cleaner, cheaper, and safer than traditional solvent extraction. As a separation technology, they have been studied for liquid/liquid separations of various solutes such as biomolecules, metal ions, and particulates (5-9).

The importance of the pertechnetate anion, TcO_4^-, in real-world separations has led us to investigate its behavior in ABS. Promising early research (1-5) indicated that the pertechnetate anion quantitatively distributes to the PEG-rich phase without complexants, while most other metal ions (including MoO_4^{2-}) stay in the salt-rich phase (5, 10-12). The partitioning behavior of TcO_4^- has been investigated as a function of salt used to generate the biphase, salt concentration, polymer molecular weight, the identity of the polymer, pH, and temperature. We have explained pertechnetate's preference for the PEG-rich phase based upon its large, polarizable nature and the small value of its estimated Gibbs free energy of hydration (ΔG_{hyd}) (13).

We have demonstrated that chaotropic anions with small $-\Delta G_{hyd}$ values will also partition to the PEG-rich phase (13), and thus when present in ABS, these ions may compete with TcO_4^- and affect its distribution ratios. The matrix ions in waste solutions cannot be neglected, and thus their influences need to be understood before ABS can be evaluated for practical use. In order to study matrix ion effects, we have chosen to examine the behavior of the halide anions on D_{Tc}. These anions represent a wide range of water-structuring to chaotropic ions, yet each has the same charge. Herein we report the results of these studies and explain our observations based upon thermodynamic aspects of the halide ion interactions with water.

EXPERIMENTAL

PEG-2000 (lot No. 00715MZ) was purchased from Aldrich and used as received. $(NH_4)_2SO_4$, NaF, NaCl, NaBr, NaI, and $NaHCO_3$ were obtained from Aldrich and were of reagent grade. NaSCN and $NaClO_4$ were of reagent grade and obtained from Fisher Scientific and The G. Frederick Smith Chemical Company, respectively. All water used was purified using a commercial deionization system. ^{99}Tc (Amersham) was purchased and used as an aqueous $NaTcO_4$ solution.

PEG-2000 solution was prepared on a weight percent basis, and the salt solutions were prepared on a molar basis. The solutions containing the matrix ions were prepared by dissolving the matrix ion in a salt stock solution and diluting with the salt stock solution to a specific concentration. Unless otherwise noted, the PEG stock solutions were 40% (w/w) PEG-2000.

The distribution ratios were measured by the following procedure. Equal volumes of PEG-2000 stock solution and salt stock solution were combined. The systems were pre-equilibrated by complete mixing for 2 min followed by 2 min of centrifugation. A tracer quantity of $^{99}TcO_4^-$ was added to the equilibrated biphasic system followed by 2 min of centrifugation, 2 min of mixing, and 2 min of centrifugation. The phases were then carefully separated and placed into separate vials. Equal aliquots of each phase were used for radiometric analyses. The radiometric distribution ratio (D) was taken as the counts per minute (cpm) in the upper PEG-rich phase divided by the cpm in the lower salt-rich phase. All measurements were carried out at least in duplicate. Radiometrically determined distribution ratios are generally accurate to ±5%; however, due to the complexity of these ABS, a conservative accuracy of ±10% is reported.

RESULTS AND DISCUSSION

Figure 1 illustrates the influences of halide ions on TcO_4^- distribution in a PEG-ABS prepared by mixing equal aliquots of 3.5 M $(NH_4)_2SO_4$ and 40% (w/w)

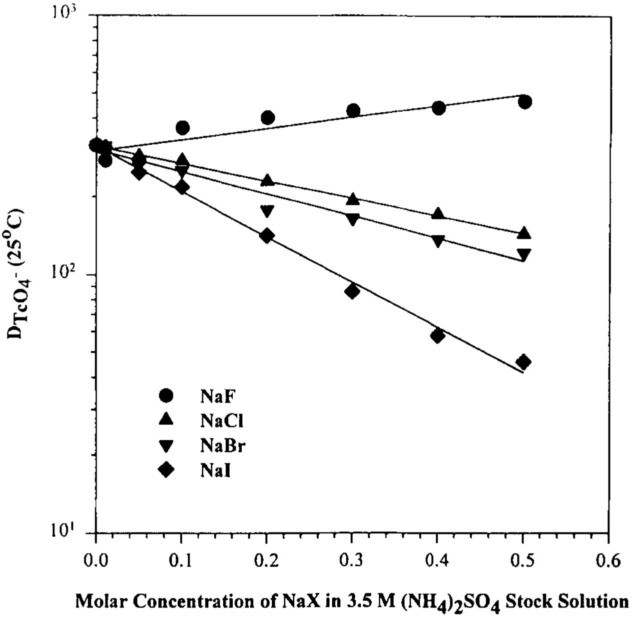

FIGURE 1. Plot of the pertechnetate distribution ratios vs. the molar concentration of halide ions in the 3.5 M $(NH_4)_2SO_4$ stock solution used to prepare the ABS with 40% (w/w) PEG-2000.

PEG-2000. The heavier halides, Cl^-, Br^-, and I^-, depress D_{Tc} in the order $I^- > Br^- > Cl^-$ with an increasingly larger effect as the matrix ions' concentrations increase. In sharp contrast to this behavior, increasing the concentration of the smallest halide ion, F^-, actually results in an increase in the distribution ratios of pertechnetate.

The negative effect on D_{Tc} values when Cl^-, Br^-, and I^- are present may result from a competition for partitioning to the PEG-rich phase between TcO_4^- and X^-. The capacity of cations in the PEG-rich phase appears to be limited (13), and the counter anions will be those which prefer this phase more. As more halide ion is introduced, the competition between TcO_4^- and X^- increases. At the tracer scale, lower distribution ratios for halide ions were observed than for TcO_4^- (13); however, increasing the amount of the halide ions in the system will result in more of these ions in the PEG-rich phase, and thus lower distribution ratios for TcO_4^- are observed.

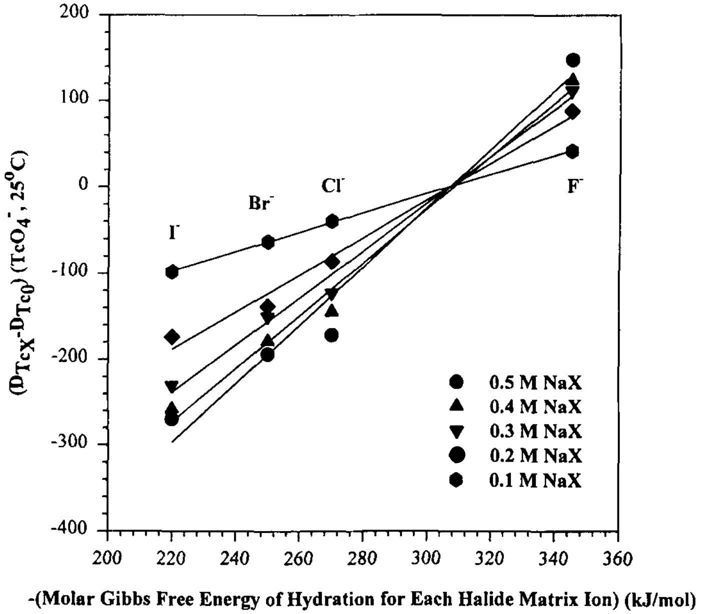

FIGURE 2. The difference in the pertechnetate distribution ratios in the 3.5 M $(NH_4)_2SO_4$/40% PEG-2000 ABS with matrix ions (D_{TcX}) and without matrix ions (D_{Tc0}) vs. the negative molar Gibbs free energy of hydration for each halide matrix ion.

We have correlated the distribution ratios for several chaotropic ions in ABS with their Gibbs free energy of hydration ($-\Delta G_{hyd}$) (13). The less negative the value of ΔG_{hyd}, the more chaotropic (water-destructuring) the ion is and the more it prefers the hydrogen bonding environment of the PEG-rich phase. The magnitude of the halide ions' influence is related to their preference for the PEG-rich phase. The greater preference the halide ion has for the PEG-rich phase, the more it depresses D_{Tc}. Iodide has the lowest $-\Delta G_{hyd}$ (220 kJ/mol), followed by Br^- (250 kJ/mol) and Cl^- (270 kJ/mol) (all ΔG_{hyd} from reference 14); thus,the halide ions' effects on the partitioning of TcO_4^- follow the order $I^- > Br^- > Cl^-$.

Of the halide ions, only fluoride is capable of salting out PEG-2000; thus, NaF(aq) can be combined with PEG-2000(aq) to form an ABS. This is not surprising

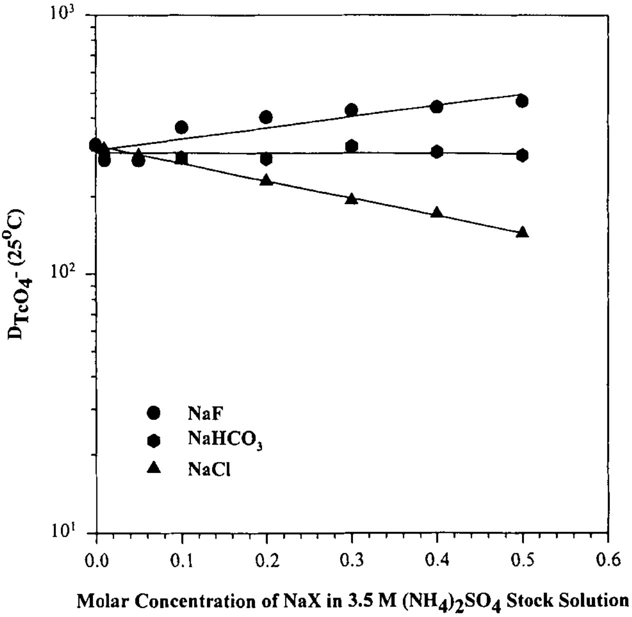

FIGURE 3. Plot of the pertechnetate distribution ratios vs. the molar concentration of NaF, NaCl, and $NaHCO_3$ in the 3.5 M $(NH_4)_2SO_4$ stock solution used to prepare the ABS with 40% PEG-2000.

due to the water-structuring nature of this ion as reflected in its large $-\Delta G_{hyd}$. As a phase-forming ion, increasing concentrations of F^- increase the incompatibility between the PEG-rich and salt-rich phases. We have previously shown that increasing the concentration of the phase forming salt results in an increase in D_{Tc} (1). The salting-out effects of anions appear to be additive and thus, of all the halide ions, increasing concentrations of F^- will actually result in increasing D_{Tc}.

Figure 2 plots the difference of distribution ratios of TcO_4^- in the 3.5 M $(NH_4)_2SO_4$/40% PEG-2000 system with (D_{TcX}) and without (D_{Tc0}) halide ions vs. Gibbs free energy of hydration ($-\Delta G_{hyd}$) of the halide ions. According to this plot, matrix ions with $-\Delta G_{hyd}$ of ~ 310 kJ/mol will have little or no influence on the partitioning of TcO_4^- for this PEG-ABS. Those matrix ions with $-\Delta G_{hyd}$ > 310 kJ/mol

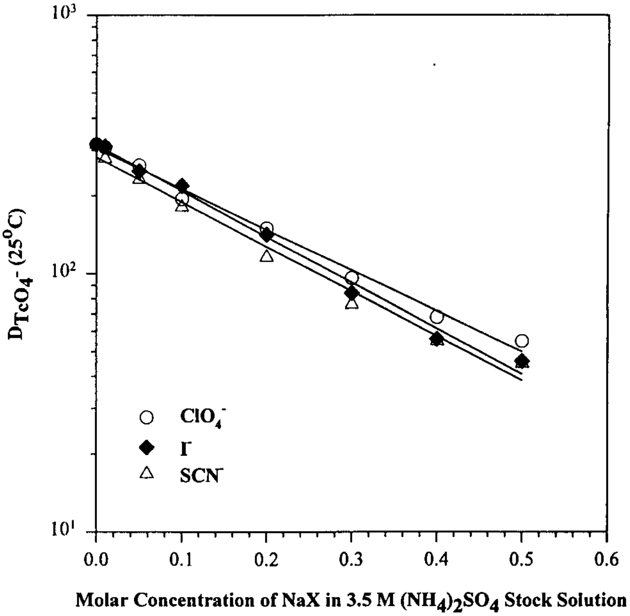

FIGURE 4. Plot of the pertechnetate distribution ratios vs. the molar concentration of NaI, NaSCN, and $NaClO_4$ in the 3.5 M $(NH_4)_2SO_4$ stock solution used to prepare the ABS with 40% PEG-2000.

will have a positive effect on partitioning of TcO_4^-, and those with $-\Delta G_{hyd} < 310$ kJ/mol will have a negative effect on D_{Tc}.

To test our hypothesis, the influence of HCO_3^- (which has $-\Delta G_{hyd} = 310$ kJ/mol (14)) on the distribution ratios of pertechnetate was investigated. The data are presented in Figure 3. As predicted, HCO_3^- has negligible influence on the partitioning of TcO_4^- in this ABS, even at relatively high concentrations.

Another useful aspect of these data is the ability to predict which salts can be used to salt-out PEG. From Figure 2, salts of anions with $-\Delta G_{hyd} > 310$ kJ/mol should form an ABS when mixed with PEG-2000. Previously we have shown that NaOH (OH^-, $-\Delta G_{hyd} = 345$ kJ/mol) in sufficient concentrations will form an ABS when contacted with PEG-2000. Sodium salts of I^-, Br^-, Cl^-, and NO_3^- ($-\Delta G_{hyd} = 275$ kJ/mol) will not form a biphase with PEG-2000 at any concentration.

According to the discussion above, the effects of matrix ions on the partitioning of TcO_4^- can be related to the ions' Gibbs free energies of hydration. If the matrix ions have similar ΔG_{hyd}, they will have similar influence on D_{Tc} in the ABS. Figure 4 illustrates the effects of three matrix ions which have similar $-\Delta G_{hyd}$ (I^-, 220 kJ/mol; SCN^-, 230 kJ/mol; ClO_4^-, 180 kJ/mol) on the distribution of TcO_4^- in the 3.5 M $(NH_4)_2SO_4$/40% PEG-2000 system. These ions have essentially the same effect in depressing D_{Tc}.

CONCLUSIONS

Matrix ions can have significant effects on the partitioning behavior of TcO_4^- in ABS. It appears, however, that these effects can be correlated to the nature of the matrix ion's ΔG_{hyd}. For the specific ABS studied here, 3.5 M $(NH_4)_2SO_4$/40% PEG-2000, those ions with $-\Delta G_{hyd} < 310$ kJ/mol depress the partitioning of pertechnetate to the PEG-rich phase while those with $-\Delta G_{hyd} > 310$ kJ/mol enhance D_{Tc}. It is not yet known whether these results can be applied to other ABS, but studies to assess this are currently underway in our laboratories.

ACKNOWLEDGEMENTS

This work was supported by the U.S. National Science Foundation Grant CTS-9207264.

REFERENCES

1. R. D. Rogers, J. Zhang, A. H. Bond, C. B. Bauer, M. L. Jezl, and D. M. Roden, Solvent Extr. Ion Exch. 13, 665 (1995).

2. R. D. Rogers, A. H. Bond, C. B. Bauer, J. Zhang, S. D. Rein, R. R. Chomko, and D. M. Roden, Solvent Extr. Ion Exch. 13, 689 (1995).

3. R. D. Rogers, A. H. Bond, J. Zhang, and C.B. Bauer, Appl. Radiat. Isot., in press (1996).

4. R. D. Rogers and J. Zhang, J. Chromatogr. B: Biomed. Appl., 680, 231 (1996).

5. R. D. Rogers, A. H. Bond, C. B. Bauer, J. Zhang, M. L. Jezl, D. M. Roden, S. D. Rein, and R. R. Chomko, In Aqueous Biphasic Separations: Biomolecules to Metal Ions, R. D. Rogers and M. A. Eiteman, Eds., Plenum, New York, 1995, pp. 1-20.

6. P. Å. Albertsson, Partition of Cell Particles and Macromolecules, 3rd ed., John Wiley & Sons, New York (1986).

7. Partitioning in Aqueous Two-Phase Systems. Theory, Methods, Uses, and Applications to Biotechnology, H. Walter, D. E. Brooks, and D. Fisher, Eds., Academic Press, Orlando (1985).

8. Aqueous Two-Phase Systems, H. Walter and G. Johansson, Eds., In Methods in Enzymology, Vol. 228, J. N. Abelson and M. I. Simon, Eds., Academic Press, San Diego (1994).

9. Poly(Ethylene Glycol) Chemistry: Biotechnical and Biomedical Applications, J. M. Harris, Ed., Plenum Press, New York (1992).

10. R. D. Rogers, A. H. Bond, and C. B. Bauer, Sep. Sci. Technol. 28, 1091 (1993).

11. R. D. Rogers, A. H. Bond, and C. B. Bauer, Sep. Sci. Technol. 28, 139 (1993).

12. R. D. Rogers, A. H. Bond, and C. B. Bauer, In Solvent Extraction in the Process Industries, Proceedings of ISEC'93, Vol. 3, D. H. Logsdail and M. J. Slater, Eds., Elsevier Applied Science, London, 1993, pp. 1641-1648.

13. R. D. Rogers, A. H. Bond, C. B. Bauer, J. Zhang, and S. T. Griffin, J. Chromatogr. B: Biomed. Appl., 680, 221 (1995).

14. Y. Marcus, J. Chem. Soc., Faraday Trans. 87, 2995 (1991).