An alternative to halogenated solvents for halogen/halide extractions

2 AUTHORS:

Steven C Petrovic
Southern Oregon University
13 PUBLICATIONS **119** CITATIONS

SEE PROFILE

George M. Bodner
Purdue University
**126** PUBLICATIONS **2,788** CITATIONS

SEE PROFILE

AN ALTERNATIVE TO HALOGENATED SOLVENTS
FOR HALOGEN/HALIDE EXTRACTIONS

Steven C. Petrovic and George M. Bodner
Department of Chemistry, Purdue University

Iodine/iodide/triiodide Equilibria

Almost 30 years ago, a physical chemistry experiment was reported in which the equilibrium constant for the following aqueous reaction was measured [1].

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$
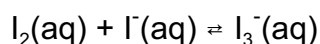
The equilibrium is established by dissolving iodine in a solution of KI of known concentration. The total I_2 and I_3^- concentration at equilibrium is determined by titrating the aqueous solution with thiosulfate [2]. The solution is then extracted with carbon tetrachloride and the I_2 concentration in the nonpolar solvent is determined by titration with thiosulfate.

The equilibrium concentration of I_2 in the aqueous solution can be calculated from the I_2 concentration in the nonpolar solvent and the distribution coefficient for the extraction of iodine between CCl_4 and water.

$$D = \frac{[I_2]_{CCl_4}}{[I_2]_{aq}} = 90$$

Glasstone [3] reports values of 85.1 - 87.5 for this distribution coefficient. We have used the value suggested more recently by Irving and Williams [4].

At this point, enough information is available to calculate the equilibrium concentrations of the three components of the reaction.

$$[I_2]_{aq} = \frac{[I_2]_{CCl_4}}{D}$$

$$[I_3^-]_{aq} = [\text{total } I_2 + I_3^-]_{aq} - [I_2]_{aq}$$

$$[I^-]_{aq} = C_{KI} - [I_3^-]_{aq}$$

These concentrations can then be used to calculate the equilibrium constant for the reaction [5].

$$K_c = \frac{\left[I_3^-\right]}{\left[I_2\right]\left[I^-\right]} = 780$$

Concern about the volume of halogenated solvent generated in this experiment recently led Sabol and Kurtz [6] to describe a method of recovering these solvents. At Purdue, we have taken a different approach to reducing the threat to the safety of both individual students and the environment from exposure to the halogenated solvents used in this experiment. At first, we simply replaced carbon tetrachloride with what we hoped were less toxic halogenated solvents, such as dichloroethane. As the list of suspected carcinogens lengthened [7], we began a search for a different category of nonpolar solvent that could be used to extract iodine from an aqueous solution. For several years, we have successfully used **p**-xylene to extract I_2 from an aqueous solution containing an equilibrium mixture of I_2, I^- and I_3^- [8]. No significant changes have to be made in the experimental procedure. The students still titrate a sample of the aqueous phase and a sample of the nonpolar phase obtained when the aqueous solution is extracted with **p**-xylene. Our results suggest that the distribution coefficient for extraction of iodine into **p**-xylene is very much larger than the corresponding constant for carbon tetrachloride.

$$D = \frac{\left[I_2\right]_{xylene}}{\left[I_2\right]_{aq}} = 436$$

When this value is used, student results agree favorably with the accepted value of the equilibrium constant for this reaction [5]. We therefore recommend considering the use of **p**-xylene for this experiment in place of a halogenated solvent.

Qualitative Analysis

Other places were **p**-xylene might replace halogenated solvents include qualitative analysis experiments, which often involve steps in which iodine and/or iodide are identified by extraction into carbon tetrachloride.

Safety

It is important to realize that substituting **p**-xylene for halogenated solvents does not replace a "toxic" material with one that is "safe." Carbon tetrachloride and chloroform are on the list of probable carcinogens proposed by the International Agency for Research on Cancer [7], whereas **p**-xylene is neither a carcinogen nor a mutagen. Xylene is flammable, however, with a flash point of $17^{\circ}C$. It also forms a harmful vapor, which may cause

dizziness, headache, nausea or mental confusion and may cause poisoning by absorption through the skin or by inhalation [9].

References

[1] Shoemaker, D. P., Garland, C. W. *Experiments in Physical Chemistry*, McGraw-Hill: New York, 1962; pp 180-184.

[2] Bassett, J., Denney, R. C., Jeffery, G. H., and Mendham, J. *Vogel's Textbook of Quantitative Inorganic Analysis*, 4th Ed., Longman: London, 1978; p. 370.

[3] Glasstone, S. *Textbook of Physical Chemistry*, 2nd Edition, D. Van Nostrand: New York, 1946; p. 740

[4] Irving, H., and Williams, R. J. P. *Treatise on Analytical Chemistry*, I. M. Kolthoff and P. J. Elving, Ed., Part 1, V. 3, Chpt 31, Interscience Publishers: New York, 1961; p. 1338.

[5] Dean, J. A. *Lange's Handbook of Chemistry*, 13th Ed., McGraw-Hill: New York, 1985; p. **5**-74

[6] Sabol, J. E. and Kurtz, D. W. *J. Chem. Ed.*, **1990**, <u>67</u>, 532.

[7] U.S. Consumer Product Safety Commission. *School Science Laboratories A Guide to Some Hazardous Substances*, U.S. Government Printing Office: Washington, DC, 1984; p. 12

[8] Bodner, G. M. *Chemistry 115-116 Laboratory Manual*, Bellwether: Edina, MN, 1990; pp 133-139.

[9] Muir, G. D. *Hazards in the Chemical Laboratory*, 2nd Ed., The Chemical Society: London, 1977; p. 432-433.