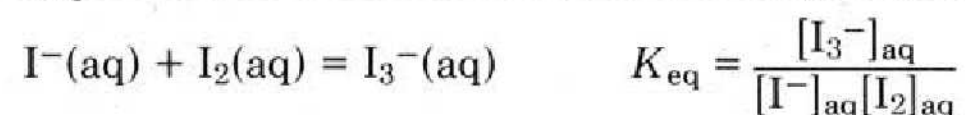
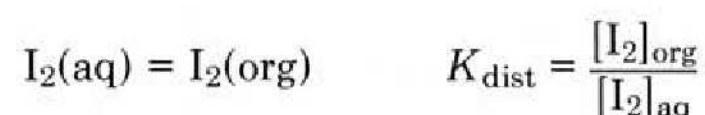


Determination of the Equilibrium Constant for Triiodide Formation: Use of a Less Toxic Solvent

The determination of the numerical value of an equilibrium constant for a selected chemical reaction is an experiment found in most general chemistry laboratory programs. An experiment of this type which appears in several laboratory manuals¹⁻³ is the determination of K_{eq} for the formation of triiodide ion in aqueous solution by the reaction



An essential feature of this experiment is the equilibration of the aqueous solution with an immiscible organic phase to establish the equilibrium



Titration of a portion of the organic phase with thiosulfate yields $[\text{I}_2]_{\text{org}}$. If K_{dist} is known, this permits calculation of $[\text{I}_2]_{\text{aq}}$. From $[\text{I}_2]_{\text{aq}}$ and titration data on the aqueous solution K_{eq} can be determined. Published versions of this experiment employ carbon tetrachloride^{1,2} or tetrachloroethylene³ as the organic phase, probably because of the well-determined literature values of 90.5 and 74.1 respectively for K_{dist} at 25°C.⁴

We have successfully used a locally written version of the triiodide experiment employing carbon tetrachloride as the organic phase. However, the exposure of inexperienced students to potentially high levels of toxic chemicals such as halogenated hydrocarbons⁵ caused us to question the continued use of this experiment in its usual form. Others may have similar reservations about this otherwise attractive experiment. Rather than abandon the experiment we sought a more acceptable organic solvent and have found that reagent grade hexanes (a mixture of isomers) can be successfully substituted as the organic phase. It meets the criteria of a workable K_{dist} value and more satisfactory exposure limits than carbon tetrachloride⁷ and is less expensive as well. Since the solvent is an isomeric mixture we measured the distribution coefficient, K_{dist} , and found it to be 35 ± 2 at 23°C under the conditions of the triiodide experiment. This compares with a value of 26 at 25°C for *n*-hexane which we calculated from the ratio of the solubility of iodine in *n*-hexane⁸ to the solubility in water.⁴ Similar calculations from the scant literature data for other saturated hydrocarbons suggests that K_{dist} increases with hydrocarbon chain length and branching.⁸ While our value of K_{dist} is not as well-defined as those for carbon tetrachloride and tetrachloroethylene, it is adequate for the thrust of the experiment.⁹ Students may also be asked to determine their own value for K_{dist} .²

A copy of our version of the triiodide experiment using hexanes as the organic phase will be provided upon request.

¹ Conroy, L. E., Tobias, R. S., and Brasted, R. C., "General Chemistry Laboratory Operations," 3rd Ed., MacMillan Publishing Co., New York, 1977, p. 201.

² Bell, J. A., "Chemical Principles in Practice," Addison-Wesley, Reading, Mass., 1967, p. 89.

³ Lippincott, W. T., Meek, D. W., and Verhoek, F. H., "Experimental General Chemistry," W. B. Saunders Co., Philadelphia, 1970, p. 201.

⁴ These values appear in the early chemical literature which is summarized in "Gmelins Handbuch der Anorganischen Chemie," Springer-Verlag, New York, 1931, Vol. 8, p. 143ff and Seidell, A., "Solubilities of Inorganic and Metal Organic Compounds," 3rd Ed., D. Van Nostrand Co., New York, 1941, Vol. I, p. 654ff. Solubility studies of iodine in other solvents are also presented in these summaries.

⁵ Standards for exposure to CCl_4 vapor are 10 ppm on a time weighted average over 8 hours, a ceiling level of 25 ppm, and a peak level of 200 ppm for 5 minutes in any four-hour period (see reference in footnote 6).

⁶ Sax, N. I., "Dangerous Properties of Industrial Materials," 4th Ed., Van Nostrand Reinhold Co., 1975.

⁷ Standards for exposure to *n*-hexane are 100 ppm on an 8 hour time weighted average with no ceiling or peak level recommendations (see reference in footnote 6).

⁸ Hildebrand, J. H., Benesi, H. A., and Mower, L. M., *J. Amer. Chem. Soc.*, **72**, 1017 (1950).

⁹ Since the temperature is not usually carefully controlled in this experiment even the well-defined K_{dist} values for the halogenated hydrocarbons do not strictly apply.

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