

The Distribution Constant of Iodine between Aqueous and Organic Phases

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The distribution of molecular iodine I_2 between two immiscible solvents such as water and carbon tetrachloride is commonly studied in undergraduate experimental physical chemistry laboratories because the equilibrium constant can be quite easily determined by a straightforward titrimetric method.

However, an organic solvent like carbon tetrachloride, which would be suitable for such studies, is classed as a "cancer-causing suspect" and its use in undergraduate teaching laboratories has been discouraged. Consequently, the relatively nontoxic octamethylcyclotetrasiloxane has been suggested as an alternative organic solvent for use in this experiment. It may be obtained from the BDH Chemical Company, Poole, England, where it is sold under the name Volasil 244. Alternatively, it may be obtained from the Alfa Aesar chemical company, 30 Bond Street, Ward Hill, MA 01835-8099 in the USA. I shall hereafter refer to octamethylcyclotetrasiloxane as Volasil for convenience. Its suitability was investigated in the present study and a value for the distribution equilibrium constant was determined. Values for the equilibrium stability constants for the complex trihalide ions I_2Cl^- and I_2Br^- were also evaluated.

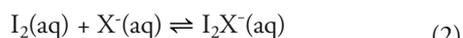
Theory

Details of the theory and experimental procedure are given in refs 1 and 2. We are concerned here with the distribution of I_2 as the solute between the two immiscible liquid phases, aqueous solution and Volasil. At equilibrium, the concentrations of I_2 in the two phases are related by a distribution constant K_D :

$$I_2(aq) \rightleftharpoons I_2(org) \quad K_D = [I_2(org)]/[I_2(aq)] \quad (1)$$

where aq represents the aqueous phase and org is Volasil. K_D is not a true thermodynamic equilibrium constant because it involves concentrations rather than activities, but it varies only slightly with the concentration of the solute. It can be determined directly by titration of both phases with standard thiosulfate solution.

However, when a solution of iodine in Volasil is thoroughly shaken with an aqueous solution of a halide (X^-), another equilibrium is simultaneously established in the aqueous phase:



$$K_S = [I_2X^-(aq)]/[I_2(aq)][X^-(aq)]$$

from which the apparent distribution constant K_D' of iodine between the two phases is given by

$$K_D' = [I_2(org)]/[I_2(aq) + [I_2X^-(aq)]] \quad (3)$$

Rearranging eq 2 we obtain (1)

$$K_D' = [I_2(org)]/[I_2(aq) + K_S[I_2(aq)][X^-(aq)]] \quad (4)$$

which from eq 1 gives

$$1/K_D' = 1/K_D + (K_S/K_D)[X^-(aq)] \quad (5)$$

In order to determine K_D and the stability constant (K_S) of the complex trihalide anions I_2X^- in water, the approximation that $[X^-(aq)]_{init} \approx [X^-(aq)]$ is made, where $[X^-(aq)]_{init}$ is the initial concentration of the halide ions. This is a good approximation for the complexes when $X = Cl, Br$ since the trihalide anions I_2Cl^- and I_2Br^- have low stabilities in water and we are using relatively large initial concentrations of the halides. Consequently, eqn 4 becomes

$$1/K_D' = 1/K_D + (K_S/K_D)[X^-(aq)]_{init} \quad (6)$$

If the above assumption holds, then a linear plot of $1/K_D'$ versus $[X^-(aq)]_{init}$ should be obtained, from which K_D may be obtained from the intercept and K_S from the slope. Error estimates for these quantities may also be evaluated from a linear least-squares calculation.

Results and Conclusions

The experiments were performed in the first-year physical chemistry undergraduate laboratories at the Cave Hill Campus of the University of the West Indies in Barbados. Solutions of I_2 in Volasil were allowed to equilibrate with aqueous solutions of the potassium halides (KCl, KBr, KI) in a water bath set at a temperature of about 23 °C. Five different concentrations of each halide were used. For KCl and KI, concentrations were in the range 0.0–2.0 M and for KBr, 0.0–0.25 M. The concentration of I_2 in each phase (as either $I_2(org)$, $I_2(aq)$, or $I_2X^-(aq)$) was determined by removing duplicate aliquots from the appropriate phase by pipet and titrating them with standard sodium thiosulfate solution. Care must be taken to ensure that the aliquots from each phase are not contaminated by the other phase. In this way K_D' was calculated using eq 3 for each halide concentration; subsequently K_D and K_S were determined from a plot of $1/K_D'$ versus $[X^-(aq)]_{init}$.

Linear plots were obtained for the I_2/Cl^- and I_2/Br^- systems but large deviations from linearity were observed for the I_2/I^- system, as noted in ref 1, making it impossible to determine K_S for the I_3^- anion by this procedure. This is probably due to the breakdown of the assumption that $I_3^-(aq) \ll I^-(aq)$.

It was found that K_D for I_2 distributed between water and Volasil is 49 ± 3 at 23 °C. This is about half the value for I_2 partitioned between water and carbon tetrachloride; for this system at 25 °C $K_D = 89.9$ (3). The value of the stability constant K_S at 23 °C for I_2Cl^- was found to be 0.90 ± 0.09 , which is in good agreement with the value of 0.96 obtained by Kahwa at 22 °C (1) and fair agreement with the value of 1.58 from the work of Benoit and Guay (4).

The value of K_S for I_2Br^- at 23 °C determined in this work was 4.5 ± 0.4 , lower than the values of 8.7 from Kahwa

(1) and 12.6 from Benoit and Guay (4). Consequently, less confidence can be placed in the value of the stability constant for I_2Br^- than for I_2Cl^- as obtained by this method. The uncertainties quoted for these experimentally determined quantities are estimated from the least-squares calculation.

Of course, it may be possible to study the temperature variation of K_S to evaluate the standard Gibbs free energy change (ΔG°) for the formation of the complex trihalide anions through the use of the relationship $\Delta G^\circ = -RT \ln K_S = \Delta H^\circ - T\Delta S^\circ$. However, this study was done primarily to establish a value for the equilibrium distribution constant for the I_2 in water–Volasil system.

In conclusion, Volasil is recommended as a substitute for carbon tetrachloride in the determination of an equilibrium distribution constant of molecular iodine between an aqueous and an organic liquid phase in student experiments, since it lacks some of the more unpleasant properties (toxicity, irritant, unpleasant smell) associated with carbon tetrachloride.

Acknowledgments

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Literature Cited

1. Kahwa, I. A. *J. Chem. Educ.* **1984**, *61*, 823.
2. Shoemaker, D. P.; Garland, C. W.; Nibler, J. W. *Experiments in Physical Chemistry*, 6th ed.; McGraw-Hill: New York, 1995.
3. Kolthoff, I. M.; Sandell, E. B.; Meehan, E. J.; Bruckenstein S. *Quantitative Chemical Analysis*, 4th ed.; Macmillan: London, 1969.
4. Benoit, R. L.; Guay, M. *Inorg. Nucl. Chem. Lett.* **1968**, *4*, 215.