

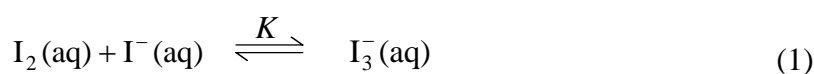
LAB 2: CHEMICAL EQUILIBRIUM (DICHLOROMETHANE – WATER)

OBJECTIVE

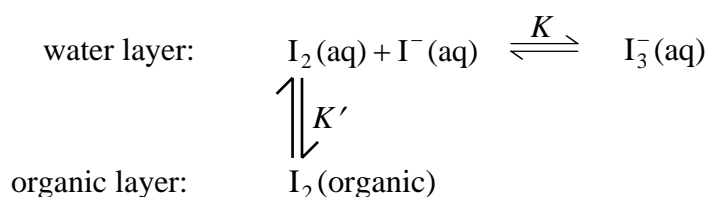
To obtain the equilibrium constant for the $I_2 + I^- \rightleftharpoons I_3^-$ system by utilizing the fact that the I_2 will distribute itself between dichloromethane and water whereas the I^- and I_3^- are soluble in the aqueous phase only.

THEORY

Iodine (I_2) is sparingly soluble in pure water but dissolves readily in aqueous solutions of potassium iodide (KI) owing to formation of complex tri-iodide (I_3^-) ions, which exist in equilibrium with free iodine molecules and iodide ions:



A complex ion, the tri-iodide (I_3^-) ion, is formed from the reaction between I^- and I_2 . In the two-phase system two equilibria occur simultaneously, each competing for I_2 :



The concentration of all species at equilibrium can be determined titrimetrically, and the equilibrium constant for the formation of the complex ion can be calculated. Titration of the aqueous layer gives the total iodine present in the aqueous layer, that is,

$$\begin{aligned} [I_2(\text{total})] &= [I_2(aq)] + [I_3^-(aq)] \\ \text{but } [I_2(aq)] &= [I_2(\text{organic})] / K' \\ [I_3^-(aq)] &= [I_2(\text{total})] - [I_2(aq)] \\ [I^-(aq)] &= [I^-(aq)]_{\text{initial}} - [I_3^-(aq)] \end{aligned}$$

The equilibrium constant (K) for the formation of the complex ion is then calculated with Eq (1). Actually the equilibrium constant should be written in terms of the activities and the activity coefficients.

$$K = \frac{[I_3^-(aq)] \gamma_{I_3^-}}{[I_2(aq)][I^-(aq)] \gamma_{I_2} \gamma_{I^-}} \quad (2)$$

However, I^- and I_3^- , with the same charge and in the same ionic environment, have very nearly the same activity coefficient, which then tend to cancel out in Eq (2). Molecular iodine (I_2) in both water and dichloromethane behaves quite ideally, so its activity coefficient is very nearly unity.

PROCEDURES

1. Prepare two 250-mL volumetric flasks, labeled **A** and **B**.

Bottle A: Measure **20.0 mL** of **0.02 M I₂** solution in dichloromethane, and **50.0 mL** of distilled water.

Bottle B: Measure **20.0 mL** of **0.02 M I₂** solution in dichloromethane, **10.0 mL** of the **0.05 M KI** solution, and **40.0 mL** of distilled water.

2. Shake both bottles vigorously for 20 - 30 minutes. Record the room temperature.
3. When equilibrium has been attained, each layer is analyzed for iodine (I₂) as follows.

Bottle A & Bottle B:

- 3.1) Perform the direct titration on the **Organic Layer** (lower phase):

- Pipet **2.00 mL** of the dichloromethane layer (lower phase) of bottle **A** and **B** into the conical flasks labelled **A1** and **B1**, respectively.
- Prepare two 100-mL beakers. Into each beaker, weigh **0.3 g** of solid KI and add **20.0 mL** of distilled water, shaking thoroughly the KI solution to mix well. Transfer each KI solution into each flask (**A1** and **B1**), and shake thoroughly.
- Titrate each solutions (in flasks **A1** and **B1**) with **0.05 M** Na₂S₂O₃ until solution becomes pale yellow in colour, then add **0.5%w/v** starch solution (an indicator). Continue the titration until the blue colour vanishes (the starch end point). Record the volume of Na₂S₂O₃ used for each solutions (in flasks **A1** and **B1**).

- 3.2) Perform the direct titration on the **Water Layer** (upper phase):

- Pipet **10.00 mL** of the water layer (upper phase) of bottle **A** and **B** into the conical flasks labelled **A2** and **B2**, respectively.
- Titrate each solutions (in flasks **A2** and **B2**) with **0.05 M** Na₂S₂O₃ until solution becomes pale yellow in colour, then add **0.5%w/v** starch solution (an indicator). Continue the titration until the blue colour vanishes (the starch end point). Record the volume of Na₂S₂O₃ used for each solutions (in flasks **A2** and **B2**).

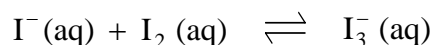
SAFETY CONSIDERATION

Solid iodine (I₂) is corrosive to the skin; its solutions stain badly.

Determination of the Iodine-Triiodide Equilibrium Constant

Lab Summary

For the reaction of iodine with iodide in water:

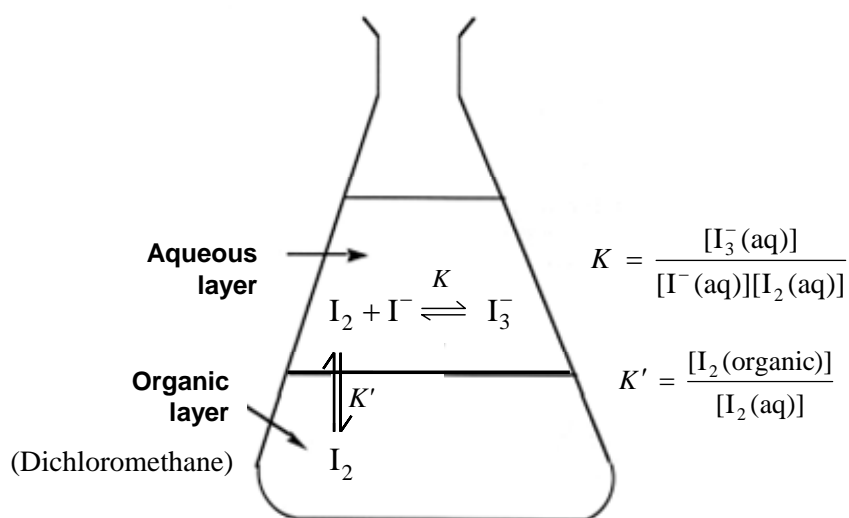


you will determine the equilibrium constant which is

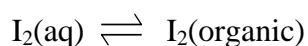
$$K = \frac{[\text{I}_3^{-}(\text{aq})]}{[\text{I}^{-}(\text{aq})][\text{I}_2(\text{aq})]}$$

Problem: To calculate K , need $[\text{I}_2(\text{aq})]$, $[\text{I}^{-}(\text{aq})]$, and $[\text{I}_3^{-}(\text{aq})]$ at equilibrium, but there is no direct method to distinguish between $\text{I}_2(\text{aq})$ and $\text{I}_3^{-}(\text{aq})$ in aqueous solution.

Approach: Solvent extraction with mineral oil since I^{-} and I_3^{-} do not dissolve in mineral oil but I_2 does.



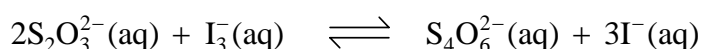
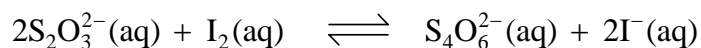
The equilibrium constant controlling the distribution of iodine between the two layers



is $K' = [\text{I}_2(\text{organic})] / [\text{I}_2(\text{aq})] = 38$

Outline of Experiment:

1. Swirl the aqueous iodine-triiodide solution with mineral oil to establish $I_2(aq)$ and $I_2(\text{organic})$.
2. Separate the mineral oil solution from the H_2O solution. Titrate the separated layers with thiosulfate. The reactions are:



3. Then

- Titrating the organic layer gives $[I_2(\text{organic})]$.
- Using K' and $[I_2(\text{organic})]$ gives $[I_2(aq)]$.
- Titrating the water layer gives $[I_2(aq) + I_3^-(aq)]$.
- Subtracting $[I_2(aq)]$ from $[I_2(aq) + I_3^-(aq)]$ gives $[I_3^-(aq)]$.
- Subtracting $[I_3^-(aq)]$ from $[I^-(aq)]_{\text{initial}}$ gives $[I^-(aq)]$.
- Having $[I_3^-(aq)]$, $[I_2(aq)]$, and $[I^-(aq)]$, calculate K .

TREATMENT OF RESULTS

1. Calculate the distribution coefficient ($K' \approx V_2/V_1$). For solutions from bottle **A**, if V_1 is the titre ($Na_2S_2O_3$) for 10.00 mL of the dichloromethane layer and V_2 that for a similar quantity of the aqueous layer.
2. Calculate the equilibrium constant (K) for the $I_2 + I^- \rightleftharpoons I_3^-$ system.

QUESTIONS

1. It has been suggested that the distribution method is likely to give results of low precision owing to mutual solubility of the two solvents, the contamination of the water layer by traces of emulsified non-aqueous layer, and a possible variation of the distribution coefficient over the concentration range studied. Discuss this statement by reference to a handle of chemical data and your own observations.
2. Describe briefly the factors which are likely to affect the position of equilibrium of reversible reactions in general and of this reaction in particular.

REFERENCES

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