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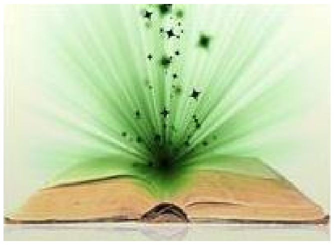

Perplexity While Comprehending the Experiment-Determination of Formation Constant of KI_3

R. Sanjeev*[1], V. Jagannadham[2] & R. Veda Vrath[3]

1.Department of Chemistry, Mizan-Tepi University, Tepi Campus, Tepi, Ethiopia
2. Department of Chemistry, Osmania University, Hyderabad-500007, India
3. Department of Chemistry, L N Gupta Evening College, Hyderabad-500002, India

Email: rachuru1sanjeev1@rediffmail.com

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ABSTRACT

"Determination of Formation constant, K_f of KI_3" is the part of the laboratory curriculum of Under Graduate programs in many Indian Universities and Colleges. Most of the students with whom we have interacted extremely intimately in the class-room and in the laboratory, either gave a perplexed expression, or they said that they were diffident regarding the conceptual comprehension of this experiment. In this article we have made an earnest effort to resolve this perplexity and the diffidence among the students.

Keywords: Distribution Coefficient, Formation Constant, Free Iodine, Bound iodine.

THEORY

The underlying theory in this experiment in the staple Indian laboratory manuals is as follows[1]:
When a saturated solution of I_2 in CCl_4 is in contact with an aqueous solution of KI in water, the following equilibrium exists in the aqueous layer:

$$KI + I_2 \rightarrow KI_3 \qquad (1)$$

or

$$I^- + I_2 \rightarrow I_3^- \qquad (2)$$

The equilibrium constant for this reaction is referred as formation constant of KI_3 (K_f) and is given by the equation

$$K_f = \frac{[KI_3]}{[KI][I_2]} \qquad (3)$$

or

$$K_f = \frac{[I_3^-]}{[I^-][I_2]} \qquad (4)$$

Thus by determining the equilibrium concentrations of KI_3, KI and I_2 in aqueous layer, formation constant can be evaluated. The value of K_f should be independent of the initial concentration of KI.

Equilibrium concentration of I_2 (in equation 3):

This can be calculated with the knowledge of distribution coefficient (K_D) of I_2 between CCl_4 and water and by determining the concentration of I_2 in CCl_4 at equilibrium. Further the aid of equation 5 is taken.

$$K_D = \frac{[I_2]_{CCl_4}}{[I_2]_{water}} \qquad (5)$$

Equilibrium concentration of I_3^-: This is equal to concentration of bound I_2, because one mole of I_2 combines with one mole of I^- to give one mole of I_3^- (equation 1). Concentration of bound I_2 is given by

$$[I_2]_{aq}^{bound} = [I_2]_{aq}^{total} - [I_2]_{aq}^{free} \qquad (6)$$

$[I_2]_{aq}^{total}$ is determined by the titration of aqueous layer with standardized sodium thiosulphate.

Equilibrium concentration of I^-:

$$[I^-]_{aq} = [I^-]_{initial} - [I^-]_{bound} \qquad (7)$$

A standard solution of KI must be taken exactly to know $[I^-]_{initial}$. The term $[I^-]_{bound}$ is equal to $[I_2]_{aq}^{bound}$ given by equation (6) of the stoichiometry of equation (1).

The experimental part consists of carefully separating the organic layer and aqueous layer and determining the iodine concentration in aqueous and organic layers using standardized sodium thiosulphate.

Perplexity: We used to ask several students the following cardinal questions which are extremely pertinent to the conceptual comprehension of the experiment:

1. What do you exactly mean by total iodine $[I_2]_{aq}^{total}$?
2. And why can't we determine the free iodine $[I_2]_{aq}^{free}$ directly by iodometric titration?
3. What is the need to know the K_D value?

The answers from most of the students involved diffidence and perplexity. The reason being the answers to the questions are extremely difficult to answer if the one reads the theory in the staple Indian laboratory manuals.

Perplexity resolved: When we titrate the aqueous layer with standardized sodium thiosulphate the titrant reacts with free iodine and when the free iodine gets exhausted, the equilibrium shifts from product to reactants side i.e. right to left abiding the Le Chatlier's principle. This process continues till the whole of KI_3 shifts towards left (theoretically KI_3 would get exhausted only at infinite time). As a consequence of this shifting of equilibrium from right to left we do not get the concentration of free iodine in aqueous layer but the total concentration of free iodine and the KI_3 formed and this is known as total iodine $[I_2]_{aq}^{total}$. Thus, the answers to questions 1 and 2 are set. Finally in order to determine the concentration of free iodine in aqueous layer, we determine the concentration of iodine in organic layer and use expression (5). This is the answer to question 3.

Calculations: Our system consists of two equilibriums as shown below:

$$\begin{tikzcd}
\mathrm{KI\ ('a')} + \mathrm{I_2\ ('c')} \arrow[r, shift left, "K_f"] \arrow[d, shift left, "K_D"] & \mathrm{KI_3\ (aqueous\ layer)} \arrow[l, shift left] \\
\mathrm{I_2\ ('b')\ \ organic\ layer} \arrow[u, shift left] &
\end{tikzcd}$$

We know that $K_D = \frac{[I_2]_{CCl_4}}{[I_2]_{water}}$ = 84 [2]

Therefore $[I_2]_{water} = \frac{[I_2]_{CCl4}}{84}$

Here 'a' is the initial concentration of KI in water layer, which is recorded at the commencement of the experiment.
'b' is the equilibrium concentration of I_2 in organic layer, which is estimated by titrating the organic layer with standardized sodium thiosulphate.
And 'c' is the total concentration of I_2 in water layer i.e.

$$\text{'c'} = [I_2]_{aq} + [KI_3]_{aq}$$

'c' is determined by titrating the aqueous layer with standardized sodium thiosulphate.
Equilibrium concentrations are calculated as follows and thus K_f determined:

$$[\ I_2]_{aq} = \left(\frac{1}{84}\right) \text{ x b} \qquad (9)$$

$$[KI_3]_{aq} = c - \left(\frac{1}{84}\right) \text{ x b} \qquad (10)$$

$$[KI]_{aq} = a - \left[c - \left(\frac{1}{84}\right) \text{ x } b\right] \qquad (11)$$

Therefore substituting equations 9, 10 and 11 in the equation 3 we get the formation constant as

$$K_f = \frac{c - \left(\frac{1}{84}\right) \text{ x b}}{\left[a - \left[c - \left(\frac{1}{84}\right) X\ b\right]\right] \text{ x } \left(\frac{1}{84}\right) \text{ x b}} \qquad (12)$$

APPLICATION

This explanation is definitely a silver bullet for the conceptual comprehension of the experiment to Freshmen studies.

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