Absorption of Iodine Vapor by Starch Granules Suspended in Potassium Iodide Solution

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The rate of absorption of iodine vapor by 0.05 M KI aqueous solution was measured and also the rate of absorption by starch granules suspended in 0.05 M KI solution. The rate was found faster when starch granules were present. Details of the measurement procedures are given.

(Zusammenfassung siehe Seite 7; Résumé à la page 7)

Introduction

The complex of iodine with starch is a well known and much studied phenomenon, but there has been no previous work on the rate of iodine absorption by starch granules.

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In many starch modification reactions as well as many other important industrial gas-liquid-particle reactions, involved is a process of absorption of a solute from a gas, through the liquid, and finally by the particles. This type of reactions is difficult to analyze because of the physical complexity of the multiple phases in addition to that of the reaction kinetics. Tsao [1, 2, 3] has recently attempted to advance a theory to explain the effect of reacting particles on the absorption of a solute. An additional purpose of
this reported experimental work is to show the presence of reacting particles (starch granules) in the liquid (KI solution) will enhance the rate of absorption of the solute (iodine) from gas phase.

Experimental

The absorption cell used is shown in Figures 1 and 2. The liquid is stirred with a magnetic stirrer at a speed such that the gas-liquid interfacial area is constant. The instrument assembly for the system is illustrated in Figure 3. A controllable amount of iodine vapor is sublimed into a known amount of gas passing through the sublimer. The mixture then flows over the surface of the solution in the absorber.

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The potentiometric method of Schoch [4] was used for measuring the iodine concentration in the aqueous solution. A Corning No. 476060 platinum electrode and a Sargent No. S-30040-15C calomel reference electrode connected to a Hewlett-Packard No. 680 strip chart recorder measured the potential changes in the aqueous solution as the iodine concentration changed.

The absorbent solution was 500 ml of 0.05 M KI in all experimental runs. Because the potentiometric method becomes insensitive at high concentrations of iodine, the maximum was 4 g/liter. The stock iodine solution was standardized using sodium arsenite as the primary standard [5].

The general procedure was first to add stock iodine solution to the absorbing solution to establish a calibration curve from which a calibration equation was obtained by fitting a polynomial to the curve. Then air, which has been blown across iodine crystals in the sublimer, was blown through the gas space above the absorbing solution and out an exhaust hole in the absorber lid. As the solution absorbed iodine, the potential changed and this change was followed on the recorder. From the calibration equation and the solution potential the amount of iodine absorbed at different times was calculated and a curve of iodine concentration versus time was plotted.

To obtain the calibration curve for the absorbent solution, 10 ml of the standardized iodine solution was pipetted into a 200-ml volumetric flask and the flask was filled to volume with distilled water. Next the diluted iodine solution (which was prepared daily due to its unstable state) was added to the absorbent solution with a 5-ml microburet in amounts sufficient to produce about a 10-mv change in the potential reading. The absorbent solution was stirred magnetically with a 2-in. stirring bar turning at 230 rpm. The 500-mv scale of the recorder was used to record the potential changes, and iodine solution was added to increase the

1 Mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.
potential in steps from its initial value to a final value of 250 mv. Beyond a total change of 250 mv, the method becomes inaccurate because the potentiometric response becomes insensitive. A typical calibration curve is plotted in Figure 4.

In an absorption run, air was blown across the iodine sublimer and then into the absorber. The amount of iodine in the air stream was determined by bubbling it through a thiosulfate solution for a known period of time at a controlled flow rate. The thiosulfate solution was then titrated with standard iodine solution. The air flow rate was more than 5,000 ml/min across a gas space of about 300 ml in volume. This rather fast flow rate ensures sufficient mixing in the gas phase inside the absorber. The iodine concentration in the air was in the range of $5 \times 10^{-4}$ mg/ml of gas and was steady during each run but varied from run to run.

The calibration curves in Figures 4 and 5 were fitted to a polynomial by the method of least squares. For the curve in Figure 4, the following equation was obtained:

$$p = -0.4707 + 7.283 \times 10^4 c + 2.729 \times 10^4 c^2 - 2.973 \times 10^6 c^3 + 3.444 \times 10^{11} c^4 - 1.212 \times 10^{13} c^5$$

(1)

where

$p =$ potential difference in mv

$c =$ iodine concentration in mg/ml.

For the curve in Figure 5 with starch present, the results are as follows:

$$p = 1.245 - 4.758 \times 10^2 c + 2.781 \times 10^4 c^2 - 1.528 \times 10^7 c^3 + 3.250 \times 10^{10} c^4$$

(2)

In an absorption run, air was blown across the iodine sublimer and then into the absorber. The amount of iodine in the air stream was determined by bubbling it through a thiosulfate solution for a known period of time at a controlled flow rate. The thiosulfate solution was then titrated with standard iodine solution. The air flow rate was more than 5,000 ml/min across a gas space of about 300 ml in volume. This rather fast flow rate ensures sufficient mixing in the gas phase inside the absorber. The iodine concentration in the air was in the range of $5 \times 10^{-4}$ mg/ml of gas and was steady during each run but varied from run to run.

When there are starch granules in the KI solution, the potentiometric response to iodine addition is different with different amounts of starch. This highly empirical characteristic of the potentiometric method requires separate calibration for different starch concentrations. A typical curve with starch present is given in Figure 5.

Figure 4. Calibration curve for 500 ml of 0.05 M KI (without starch).

Figure 5. Calibration curve for 1.0 gm cornstarch in 500 ml of 0.05 M KI.

Figure 6. Drawing of typical recorder response (without starch).

For the absorption runs with starch added, the experimental work was much more tedious. A typical recorded curve is shown in Figure 7. Complexing between iodine and granular starch is apparently not instantaneous. It seemed to proceed by a fast adsorption of iodine on the surface of
the starch granule followed with a relatively slow iodine diffusion into the interior of the granules before the iodine finally complexes with the helical structures of the starch molecules. Detailed descriptions of the iodine-starch reaction are available elsewhere [6]. This mechanism means that an instantaneous potentiometric reading, such as the one in Figure 7, does not represent a steady state iodine concentration. Instead, one has to wait for the system to reach an equilibrium after exposure (45 seconds in Figure 7). Only from the equilibrium potentiometric reading can one get the iodine concentration from a calibration curve. The flat region in Figure 7, after a long wait, indicates the establishment of the equilibrium. From the potentiometric reading at equilibrium, a value of iodine concentration was obtained. For a complete curve of iodine absorbed versus time, it is necessary to make several runs identical except for exposure times.

Iodine concentration is plotted versus time of exposure (or absorption time) in Figure 8 and again in Figure 9. The rate of iodine absorption is obtained from such figures. In both figures, the relationship is linear.

Absorption runs without added starch did not produce straight line relationships, particularly during the latter part of each absorption run. Typical results are plotted in Figure 10. After a long exposure, the relationship tends to show curvature.

The results in Figures 8 and 9 can be fitted with the following equation:

\[
\frac{c}{c_{eq}} = k_1 t + b_1 \quad (3)
\]

where \(c_{eq}\) = iodine concentration in the gas, and \(t = \) time. The values of \(k_1\) and \(b_1\) for these two figures are:

<table>
<thead>
<tr>
<th>wt. starch, gm</th>
<th>(k_1), sec(^{-1})</th>
<th>(b_1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.217</td>
<td>-1.97</td>
</tr>
<tr>
<td>1.0</td>
<td>0.174</td>
<td>1.15</td>
</tr>
</tbody>
</table>

To compare the absorption rates in runs made with and without starch in the KI solution, values of \(c\) for the absorption runs with starch were calculated using Equation 3 with the same \(c_{eq}\). This comparison is illustrated in Figure 10. To compare the rates of absorption, results such as those in Figure 10 were graphically differentiated and
plotted as in Figure 11. For all the absorption data, the rate of absorption was faster with starch granules suspended in the KI solution than without. Additional data appear in an MS thesis by Freeman [7].

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**Zusammenfassung**


**Résumé**

Absorption de vapeur d'iode par des grains d'amidon suspendus dans une solution d'iode de potassium. La vitesse d'absorption de vapeur d'iode par une solution aqueuse d'iode de potassium (KI), 0,05 molaire, ainsi que la vitesse d'absorption par des grains d'amidon, suspendus dans une solution de KI 0,05 molaire a été mesurée. La vitesse était plus importante en présence des grains d'amidon. Les détails concernant les procédés de mesure sont donnés.

**References**


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