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Diffusion of sulfuric acid in protective organic coatings

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Abstract

Organic protective coatings and linings are widely used to prevent corrosion in industrial processes. However, the permeation of aggressive chemicals through coatings can induce failures. These are described in the literature, but rarely quantified. To measure the diffusion rates of aggressive chemicals through organic coatings, a diffusion cell was designed. The diffusion cell designed is simple, small and suitable for scaling up to a battery of cells. A concentration profile of H\textsubscript{3}O\textsuperscript{+} through epoxy coatings was achieved for sulfuric acid aqueous solutions, which can be used to estimate diffusion coefficients of H\textsubscript{3}O\textsuperscript{+}. Typically, Crank’s time-lag method is used to estimate the diffusion coefficients but more complicated modelling is required for sulfuric acid solutions. Future modelling work is needed to estimate diffusion behavior of sulfuric acid.

Introduction

Organic protective coatings and linings are widely applied to protect metals in various industrial processes working with highly aggressive chemicals [1]. The basic protective mechanism is a barrier effect, impeding the transport of aggressive chemicals and preventing contact with the substrate [2]. Water and/or aggressive chemicals permeate through coating systems and, subsequently, reactions will occur at the substrate/coating interface initiating corrosion [3]. The reactions can result in cathodic disbondment, which is one of the major modes of failure of organic coatings [4].

It is important to know the diffusion rates of aggressive chemicals through organic coatings in the design and selection of protective coatings. Studies have been performed to determine the diffusion rate of chemicals through coating systems [4-8]. In addition, diffusion cells using time-lag methods have been designed to obtain diffusion coefficients of chloride ions through organic coatings [4]. Also, diffusion coefficients of acids through epoxy resins have been estimated by a microscopic method using the Einstein diffusion-mobility relationship [6-8]. In this study, a diffusion cell was designed and constructed to measure the permeation of H\textsubscript{3}O\textsuperscript{+} for sulfuric acid solutions through organic coatings. The diffusion cell designed is a compact and simple set-up for monitoring concentration profile.

Experimental

The two-chamber diffusion cell (cell A), as shown in Figure 1, is used to estimate the diffusion coefficient of sulfuric acid through an amine-cured novolac epoxy film. The diffusion cell consists of two chambers: feeding chamber (right) and receiving chamber (left). The feeding chamber is designed to contain an aqueous solution of sulfuric acid while the receiving chamber contains distilled water. The epoxy coating sample is placed between the two chambers. An Elcometer 355 thickness gauge is used to measure the coating thickness. A pH sensitive electrode, Metrohm Combined pH glass electrode, is inserted into the receiving chamber to continuously monitor the pH change of the solution inside. The Metrohm pH Meter continuously records the pH. A 10 wt.% sulfuric acid solution is added into the feeding chamber from the feeding hole. The feeding chamber is loosely sealed with a rubber stopper and the feeding hole of the receiving chamber is loosely sealed with the electrode. This ensures that both chambers are in contact with the atmosphere, which prevents the development of an osmotic pressure. The whole set-up is placed in a fume-hood at 21±2 °C.
Figure 1: Cross-section scheme of diffusion cell (cell A) and the coating sample between two chambers.

Mathematical model
The diffusion of sulfuric acid through coating systems is complicated. Sulfuric acid is a diprotic acid and has two dissociation steps as shown in Equation (1) and (2). Crank’s time-lag method is not sufficient to describe the diffusion process of sulfuric acid and the requirement of electroneutrality has to be considered. A detailed mathematical model is needed to describe the diffusion process of sulfuric acid and will be developed in future work.

\[
\begin{align*}
\text{H}_2\text{SO}_4 + \text{H}_2\text{O} & \rightleftharpoons \text{H}_3\text{O}^+ + \text{HSO}_4^- \\
\text{HSO}_4^- + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2\text{O}^+ + \text{SO}_4^{2-}
\end{align*}
\]

Results and discussion
Carneiro et al. (2006) [5] designed a permeation cell (cell B) to estimate the diffusion coefficient of chloride ions through coating films as shown in Figure 2. A difference between cell B and cell A of the present work (see Figure 1) is the orientation of the set-ups. Cell A works horizontally so that no air bubbles are trapped inside the chambers and a water container (see Figure 2) is not needed for cell A. Due to the large permeation area in cell B, Kraft paper is required to support the coating sample. However, it is feasible to use free films in cell A because the diameter of the coating sample is only 4 cm. The volume ratio of the upper chamber to that of the lower chamber is around 3 for cell B, while it is around 6 for cell A. The concentration in the feeding chamber will not be diluted as much for cell A as for cell B. Stirring is not required in cell A because the diffusion rate of sulfuric acid in water is around $2 \times 10^{-9}$ m$^2$/s [10] that is, 5 orders of magnitude larger than that in the coating. It is reasonable to assume that the concentration in the receiving chamber is homogeneous.

Figure 2: Cross-section scheme of chloride ion permeation cell (cell B) [5]
As shown with an example in Figure 3, pH change in the receiving chamber is continuously monitored and subsequently used to calculate the concentration of $\text{H}_3\text{O}^+$. The concentration development in the receiving chamber can be divided into two stages: a non-steady state and a steady state. During the non-steady state, there is a slight pH increase after the initial pH drop, which might result from the dissolution of amines from the coating sample. During steady state, the concentration of $\text{H}_3\text{O}^+$ increases linearly so that the flux of $\text{H}_3\text{O}^+$ through the coating is constant. Reported literature values for diffusion coefficients of sulfuric acid through epoxy coatings are listed in Table 1. These values can be used for future comparison when diffusion coefficients for sulfuric acid solution are estimated.

**Table 1: Literature values for diffusion coefficients of sulfuric acid through epoxy coatings**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Coating systems</th>
<th>Solution concentration</th>
<th>Diffusion coefficients ($\text{m}^2/\text{s}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Epoxy Amine</td>
<td>$\text{H}_2\text{SO}_4$ 8 wt.%</td>
<td>$2\times10^{-17}$</td>
<td>[6]</td>
</tr>
<tr>
<td>2</td>
<td>Epoxy Amine, 12% chip shaped fillers</td>
<td>$\text{H}_2\text{SO}_4$ 8 wt.%</td>
<td>$3.02\times10^{-14}$</td>
<td>[7]</td>
</tr>
<tr>
<td>3</td>
<td>Epoxy F</td>
<td>$\text{H}_2\text{SO}_4$ 10 wt.%</td>
<td>$1.42\times10^{-14}$</td>
<td>[3]</td>
</tr>
<tr>
<td>4</td>
<td>Epoxy Novolac</td>
<td>$\text{H}_2\text{SO}_4$ 10 wt.%</td>
<td>$1.66\times10^{-15}$</td>
<td>[3]</td>
</tr>
</tbody>
</table>

**Conclusions**

The diffusion cell designed can be utilized to estimate diffusion coefficients of chemicals through organic coatings if a proper probe is used to indicate the concentration change in the receiving chamber. Future modelling work is needed to estimate diffusion coefficients for sulfuric acid (i.e. for $\text{H}_3\text{O}^+$, $\text{HSO}_4^-$, and $\text{SO}_4^{2-}$). The designed diffusion cell is simple and easily constructed, and it only requires an ion sensitive probe to conduct diffusion tests. However, there is still a need for improvements on the current diffusion cell. Issues, such as evaporation of water need to be handled. An updated diffusion cell will be designed and constructed to get a better estimation of diffusion coefficients.
Acknowledgements
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References