

## Response and Sorption Studies on Glass Electrodes in Isopropanol

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Prolonged storage of hydrated glass electrodes in air and in isopropanol was shown to degrade the hydrogen ion response. On the basis of C14-labelled isopropanol experiments, it was concluded that sorption of this solvent did not influence the electrode response. Sorption effects were observed on etched glass, probably originating from solvent inclusions on the rough surface, while on the smooth hydrated glass surface no sorption could be detected. The lithium ion flux from the hydrated glass into isopropanol was about ten times less than that into water. The low lithium ion flux, as well as the slow electrode response, were explained by the dehydration of the gel-layer.

The hydrogen ion response of common glass electrodes is extremely fast.<sup>1-3</sup> However, prolonged storage in organic solvents may cause a sluggish response. In some instances the rapid response was shown to be restored when the electrode was immersed in water.<sup>4,5</sup> A certain amount of water seems to be necessary for a good electrode response in non-aqueous solutions, and therefore a dehydration of the glass surface will cause a slow response.

In an aqueous solution the hydrogen ion selective lithia glass hydrates continuously resulting in a layer in which the lithium ions are replaced by hydrogen ions.<sup>6</sup> The gel-layer has been described as a region located between two moving boundaries. The external boundary, solution/gel-layer, moves inwardly due to dissolution. The internal boundary, gel-layer/bulk glass, moves inwards towards the interior glass at a rate determined by the lithium-hydrogen ion exchange and the diffusional influx of water. During the first two weeks of hydration the internal boundary moves faster than the external boundary, *i.e.*, the gel-layer grows thicker.

In non-aqueous solutions the hydration process is probably retarded; inhibition has been found in isopropanol.<sup>7</sup> The flux of lithium ions from the glass into the solution markedly decreased when a hydrated electrode was transferred from water to isopropanol. It was also observed that the gel-layer stopped growing thicker. The reactions involved in the hydration processes

in water thus cannot proceed in isopropanol in the same way. However, other interactions with the gel-layer must not be excluded. In methanol, for instance, Folman and Yates<sup>8-10</sup> have studied the adsorption by interferometric and infrared spectroscopic methods. They concluded that adsorption of solvent molecules occurred on the hydroxyl groups as well as on other sites, assumed to be oxygen or silicon atoms. On amorphous silica, Lowen and Broge<sup>11</sup> have suggested an esterification of the hydroxyl groups by alcohols. This reaction changed the surface properties in a manner similar to dehydration.

On interpreting the delayed response behaviour of glass electrodes in non-aqueous solvents, the effect of dehydration alone has been emphasized. Solvent interactions with the gel-layer might change the electrode properties in a similar way. This study has been undertaken to investigate whether the slow response of glass electrodes is a consequence of solvent sorption.

### EXPERIMENTAL

*Response studies.* An Ingold LoT electrode was placed in a thermostatted vessel (25°C) containing 20 ml of a  $10^{-4}$  M picric acid isopropanol solution. 2 ml of a  $10^{-2}$  M picric acid isopropanol solution were rapidly added from a syringe to the solution in the vessel. stirring was provided with a motor-driven glass propeller. An Ag/AgCl reference electrode was used. It was placed in a PVC tubing with a dialysis film at the bottom. The potential changes were recorded on a Mosley 680 recorder. The glass electrode pre-treatments are described below. By this procedure a step-wise change of hydrogen ion activity was produced. An ideal electrode should produce a voltage step output. The rise of the recorded voltage can be taken as a measure of electrode response rate.

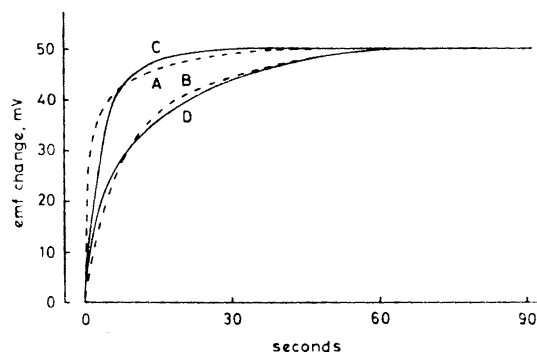
*Sorption studies.* Semi-spherical bulbs made of Ingold LoT glass were used. Etched and hydrated bulbs were investigated. Etched glass bulbs were obtained by immersion in a 5 % hydrofluoric acid solution for 2 min. Hydrated electrodes were etched as above and then hydrated for two days in water. The bulbs were placed in isopropanol-1,3-C14 (The Radiochemical Centre, Amersham) with a specific activity of 0.05 mCi/g. After different storage times they were rinsed in four 10 ml portions of inactive isopropanol, half a minute in each portion. This rinsing procedure was shown to be satisfactory, since background activity was obtained in the last two rinsing portions. After the rinsing procedure, the bulbs were etched in 2 ml of a 5 % hydrofluoric acid solution for 1 min. An aliquot of 1 ml was taken and diluted with 10 ml of Bray's solution.<sup>12</sup> The samples were counted in a Packard Liquid Scintillation Spectrometer, Model 3375. The blank consisted of 1 ml hydrofluoric acid (5 %) and 10 ml Bray's solution.

*Leakage studies.* Semi-spherical bulbs of Ingold LoT glass, hydrated for 3 days, were stored in 10 ml inactive isopropanol during about one day and then transferred to a new 10 ml isopropanol portion for another day's storage. The samples were analysed for lithium by flame emission spectroscopy.

### RESULTS

In Fig. 1, the response of the low temperature electrode Ingold LoT is shown for different pre-treatments of the electrode surface. Curve A has been obtained after etching the electrode in a 5 % HF solution for 2 min. Such a treatment removes the entire gel-layer.<sup>13</sup> The response to the hydrogen ion concentration change is fast.

Curve B shows the response of a hydrated electrode, which was stored in air (about 35 % relative humidity) for 7 days. The response is obviously quite



*Fig. 1.* Hydrogen ion response of an Ingold LoT electrode in isopropanol after different pre-treatments. The picric acid concentration was rapidly increased from  $10^{-4}$  M to  $10^{-3}$  M. A, etched electrode; B, air-stored hydrated electrode (7 days); C, hydrated electrode (aqueous storage); D, hydrated electrode stored in isopropanol for several months.

slow. Curve C has been obtained after immersion of the air-dried electrode in an aqueous pH 7 buffer for 2 h. It can be seen that a fast response results from this treatment. Further storage in the aqueous buffer solution did not change the response characteristics of this electrode.

Curve D illustrates the response of the hydrated Ingold LoT electrode after storage in pure isopropanol for several months. The response is retarded by this treatment.

*Table 1.* Amounts of isopropanol sorbed on glass bulbs at different states. Average area of the bulbs:  $3 \text{ cm}^2$ .

Glass state	Average amount of 2-PrOH (mol)	Number of observations	Rel. standard dev. (%)
Etched	$2 \times 10^{-8}$	5	29
Hydrated	$< 6 \times 10^{-9}$	5	—

Table 1 shows the average amounts of isopropanol sorbed by etched and hydrated glass bulbs. The bulbs were stored for various times in isopropanol, but no significant time dependence in the region 0.5–144 h was found in any case. The average values have therefore been calculated from the analysis results obtained at different storage times. For hydrated glass bulbs, blank values were obtained in all cases. The detection limit of the method was  $6 \times 10^{-9}$  mol isopropanol when defined as the double blank value. The average area of the glass bulbs was estimated to be  $3 \text{ cm}^2$ .

Table 2 gives the amounts of lithium ions leached from hydrated Ingold LoT glass bulbs into inactive isopropanol as well as into water. As can be seen, the amount of lithium ion leakage into water is considerably higher.

Table 2. Amount of Li<sup>+</sup> leached into water and isopropanol from hydrated Ingold LoT glass bulbs. At zero time in the table the bulbs have been hydrated for 3 days in water.

Time period h	Amount of Li <sup>+</sup> (mol) leached into water	Amount of Li <sup>+</sup> (mol) leached into isopropanol
0–24	$1.5 \times 10^{-7}$	$9.0 \times 10^{-9}$
24–48	$1.3 \times 10^{-7}$	$8.5 \times 10^{-9}$

### DISCUSSION

From Fig. 1 it can be concluded that both isopropanol and air storage of the hydrated Ingold LoT electrode caused a slow response. Both electrode pre-treatments will certainly remove water from the gel-layer. Since water molecules facilitate the transfer of hydrogen ions, the removal itself may be the cause of the response behaviour. However, an isopropanol sorption on the glass surface may influence the response in a similar manner. Absence of water might favour an adsorption of the alcohol on hydroxyl and possibly other sites analogous to that of methanol as described by Folman and Yates.<sup>8–10</sup>

A comparison of the results given in Fig. 1 and in Table 1 shows that no correlation between the amount of sorbed isopropanol and the response behaviour exists. On the etched glass surfaces a certain sorption was found while on hydrated surfaces no sorption could be detected. In spite of this, the response was very fast for both electrode states. It is therefore very likely that the sluggish response behaviour is caused by the desorption of water and that isopropanol sorption has no influence.

In order to explain the difference in sorption ability between etched and hydrated glasses their surface structures must be examined. By using electron scanning microscopy it has been established that pits appear on the etched glass while the hydrated glass exhibits a relatively smooth surface.<sup>6</sup> The detection limit of the method used corresponds to 4–5 monolayers of isopropanol if the surface area is 3 cm<sup>2</sup> and if only adsorption is accounted for. The amount of isopropanol found on etched glass was so large that effects other than adsorption (or esterification of surface sites) must be present. The main contribution to the measured sorption probably originates from solvent inclusions within porous etch-spots on the rough surface. A deeper penetration into the bulk glass is most unlikely since there is no detectable penetration into the hydrated glass surface. Penetration into a hydrated glass surface occurs more easily than into an etched surface.<sup>13</sup>

There are several indirect reports that the reactions between the glass network and water result in a loose gel-layer structure.<sup>13–16</sup> Solvent penetration into the gel-layer might thus be possible. The gel-layer thickness has been estimated to be about 1000 Å on an Ingold LoT electrode hydrated for two days.<sup>17</sup> The amount of isopropanol detected by the method used here corresponds to one solvent molecule per hundred ion exchange sites. Since every isopropanol analysis on the hydrated glass resulted in blank values it may be concluded that no detectable penetration of isopropanol into the gel-layer had occurred.

A high concentration of water in the external part of the gel-layer is to be expected on the hydrated Ingold LoT glass in conformity with the findings on sodium glasses.<sup>15</sup> As can be seen in Table 2, the amount of lithium ions leached during a certain time period in isopropanol is low compared with corresponding leakage in water. This observation is equivalent to a lower hydrogen ion flux inwards towards the glass bulk. As no isopropanol penetration was obtained, the cause of the decrease in hydrogen ion flux should be the absence of enough hydrogen ions and/or water molecules. The presence of water molecules in the gel-layer facilitates any ion transport. The water in the gel-layer will gradually be depleted due to diffusion out to the solvent and due to the continuous reaction with the dry glass. The depletion of water will slow the rate of hydrogen ion transfer which should lead to a retarded response, as observed for the electrode stored in isopropanol (curve D in Fig. 1).

*Acknowledgements.* The authors thank Dr. W. Ingold, Zürich, for gifts of specially made glass bulbs, Professor G. Johansson for valuable discussions and Dr. M. Sharp for linguistic revision of the manuscript.

This work was supported by grants from the *Swedish Natural Science Research Council*.

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Received January 11, 1973.