cell (H) that appears to be related to the wurtzite-type (II) cell according to the relations

$$a_H \cong 2a_{II},$$
$$(h00)_{II} = \tfrac{1}{2}(h00)_H,$$
$$(hk0)_{II} = \tfrac{1}{2}(hk0)_H$$

where $a_{II} = 4.59$ Å, $c_{II} = 7.51$ Å, $a_H = 9.20$ Å, and $c_H = 9.02$ Å. There does not appear to be any relation between the c-directions of the two structures. Constants for two other cells, tetragonal (T) and orthorhombic (O), can be derived from the hexagonal one according to the relations

$$a_T \cong (a_H + c_H)/2 \qquad a_T = 9.14 \text{ Å}$$
$$c_T = (\sqrt{3}/2)a_H \qquad c_T = 7.98 \text{ Å}$$

and

$$a_O = 1.055\, a_T \qquad a_O = 9.37 \text{ Å}$$
$$b_O = 0.892\, a_T \qquad b_O = 8.15 \text{ Å}$$
$$c_O = a_H \qquad c_O = 9.20 \text{ Å}$$

Indexing of the three cells can be accomplished with nearly the same degree of fit, and therefore the indices for all three are presented in Table 1. The measured specific volume of phase II at 1 atm is 0.1759 cm³/g, and for phase III at 3 kb, 0.1431 cm³/g. In view of the specific volume of these cells with Z equal to 12 molecules per cell, as presented in Table 1, the orthorhombic cell appears to be the most acceptable. For the tetragonal cell, Z equal to 10 gives a specific volume of 0.1711 cm³/g, a possibility that as yet cannot be ruled out.

It is our suggestion that any further attempt to obtain x-ray diffraction data for this phase should be carried out in an apparatus employing perfectly hydrostatic pressures. We have made several unsuccessful attempts to obtain the phase IV diffraction pattern using the beryllium Bridgman anvil apparatus (*12*, Fig. 1*A*). The narrow range of stability of the form combined with the pressure gradient of such devices results in such a small quantity converted [approximately 15 percent in the anvil shown in Fig. 1 of the Van Valkenburg paper (*9*)] that it is difficult to obtain definitive x-ray diffraction patterns. It is evident, however, that pressure gradients in the anvil device can be considerably reduced by cycling the pressure up and down until there is no more extrusion of the sample (*9*, p. 97).

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23 OCTOBER 1964

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13 July 1964

Effect of Traces of Large Molecules Containing Nitrogen on Hydrogen Overvoltage

Abstract. *Organic amines, present in very small concentrations (below 10^{-6}M) in 0.1N H_2SO_4, cause a significant increase in hydrogen overvoltage, the effect being stronger the higher the molecular weight. The increase could be accounted for by the usual site-blockage concept. In the case of egg albumin, a drastic increase of over 300 mv was observed at 12.5 ma/cm² for a concentration of only 0.01 part per million. A new mechanism is proposed in which the dielectric constant and hydrogen-ion activity are believed to be depressed in a region twice as thick as the usual transition region.*

Hydrogen overvoltage is defined as the difference between the potential of an electrode at which hydrogen is being evolved at a given current density and the potential of a standard (reversible) hydrogen electrode in the same solution (*1*). While the current flows between the working hydrogen electrode and an anode elsewhere in the solution, the overvoltage is measured between the working hydrogen electrode and a standard reference electrode by means of a Luggin capillary at the surface of the working electrode.

The magnitude of the hydrogen overvoltage in acid solutions has been attributed largely to the kinetics of transfer, discharge, and recombination reactions involving the cathode and the so-called "Stern" double layer (*2*) which acts like a capacitor. Beyond the Stern double layer is a diffusion-controlled polarization layer which is diluted during electrolysis. Both the Stern and polarization layers introduce resistance giving rise to an "IR drop" voltage. Generally, for small and moderate current densities, and under agitation, it appears justifiable to neglect the IR drop (*3*), as is implied when the measured overvoltage is calculated from the electrode kinetics. In the presence of impurities or contaminants, hydrogen evolution usually occurs at a higher overvoltage than it does when the surface is scrupulously clean (*3*, p. 131). This effect is known as "poisoning" (*4*). While such poisoning effects have been known for a long time (*1*, *5*), little work appears to have been done in measuring the effect of trace amounts (10^{-6} to $10^{-8}M$) of organic compounds with large molecules in aqueous solution. Yet such results would have both practical and theoretical implications. We have found that amines of high molecular weight, at these low concentrations, can significantly affect the overvoltage at a lightly platinized electrode, and that egg albumin at 0.01 ppm increases it drastically. We believe that these results shed new light on the mechanism of interaction of organic compounds with a hydrogen electrode, and suggest a possible explanation for this effect.

Our studies were made in both a large (500 ml) unstirred all-glass cell and in a small (15 ml) flowing cell. The flowing cell was also constructed entirely of glass, with adjustable cathode-to-reference spacing and provision to vary the flow rate from 0 to 10 ml/sec. Both cells were operated under a hydrogen atmosphere with 0.1*N* H_2SO_4 as the standard electrolyte; data were recorded on a Sanborn model 150 recorder.

In Fig. 1 the overvoltage is plotted as a function of current density for a number of organic amines and quaternary ammonium compounds. The shaded area A indicates the reproducibility of control runs with no added organic compounds for both types of cell. Tetramethylammonium bromide (TMAB) (cation equivalent weight 72) and ethanolamine (equivalent weight 61) did not produce an increase in hydrogen overvoltage which fell outside the

shaded area at concentrations as high as 10^{-3} equivalents per liter.

Di-*n*-heptylamine (equivalent weight 215) (Fig. 1, curve *B*) produces a relatively small increase in overvoltage at a concentration of $2 \times 10^{-7}M$, but not below this concentration. Dodecylbenzyldimethylammonium chloride (DBDA), a surface-active quaternary ammonium compound, causes a substantial increase in hydrogen overvoltage even when present in concentrations as low as $10^{-8}M$ (curve *C*). Increasing the concentration of DBDA (curve *D*) increases the hydrogen overvoltage further, an effect which is also found with di-*n*-heptylamine. Curve *E* shows the remarkable sensitivity of the electrode to egg albumin, which was present at a concentration of 0.01 ppm, or about 10^{-8} equivalents per liter (eq/liter), if an equivalent weight of 1100 is assumed (*6*).

Among the most sensitive techniques we found for detecting the effect of the organic trace on the overvoltage was to add the trace at a relatively high current density. Tetramethylammonium bromide produced no visible change in overvoltage (less than 2 mv), even at $10^{-3}M$. Di-*n*-heptylamine produced an increase of 5 mv with increase in concentration from $3 \times 10^{-6}M$ to $1 \times 10^{-5}M$; the change occurred within 30 seconds, and the overvoltage remained constant thereafter for nearly 15 minutes. Similar behavior was observed for DBDA, but at lower concentrations and over a somewhat longer period: $2 \times 10^{-7}M$ produced an immediately detectable shift, with about 120 seconds required for the overvoltage to stabilize.

Albumin, on the other hand, showed two marked differences in behavior, and these can be seen in both Figs. 1 and 2. First, in Fig. 1, at the lowest concentration tested, 0.01 ppm (about 10^{-8} eq/liter), an increase of over 250 mv was observed at 6.5 ma/cm^2; this increase exceeded 300 mv at 12.5 ma/cm^2 (Fig. 2). Second, the maximum rate of change was not reached for more than 5 minutes, and after 15 minutes it was still increasing at a rate of 10 mv/min.

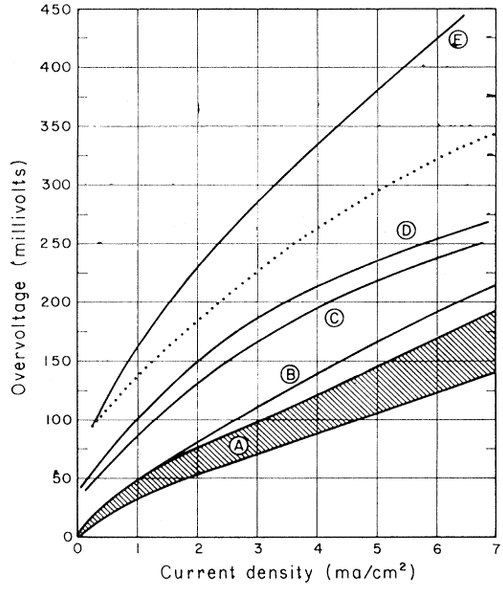
In general, poisoning of the electrodes cannot be reversed by replacing the contaminated electrolyte with fresh, uncontaminated solution, indicating strong adsorption. Anodic cleanup by reversal of polarity is effective if currents in excess of 10 ma/cm^2 are used for 5 to 10 minutes, followed by removal of oxygen from the solution.

In order to understand how it is possible for trace amounts of material to cause such large effects, it is necessary to study the films at the electrode surface. In the absence of agitation the diluted polarization layer can be as thick as 0.05 cm (*3*, p. 146). The resulting concentration overvoltage can be written:

$$\eta^o = \frac{0.059}{Z} \log \frac{C}{C^0} \qquad (1)$$

where C and C^0 are, respectively, the hydrogen-ion concentrations in the film and in the bulk, and Z is the ionic charge. Previously, it has been assumed that there are no differences in activity coefficients between the polarization film and the bulk solution; estimates of the diffusion overvoltage based on this assumption are of the order of hundredths of a volt (*7*).

According to the calculations of Conway, Bockris, and Ammar (*8*), the dielectric constant of the rigid Helmholtz portion of the Stern layer (which may be estimated at 2 Å in thickness) is less than 10, compared with about 80 in the bulk; and the dielectric constant of the outer portion of the Stern layer (the so-called "Gouy" portion) rises from about 40 at a distance of about 5 Å to the bulk value of 80 at a distance of about 25 Å from the electrode. These numbers apply to solutions containing 0.1 gram-ions per liter. Thus,



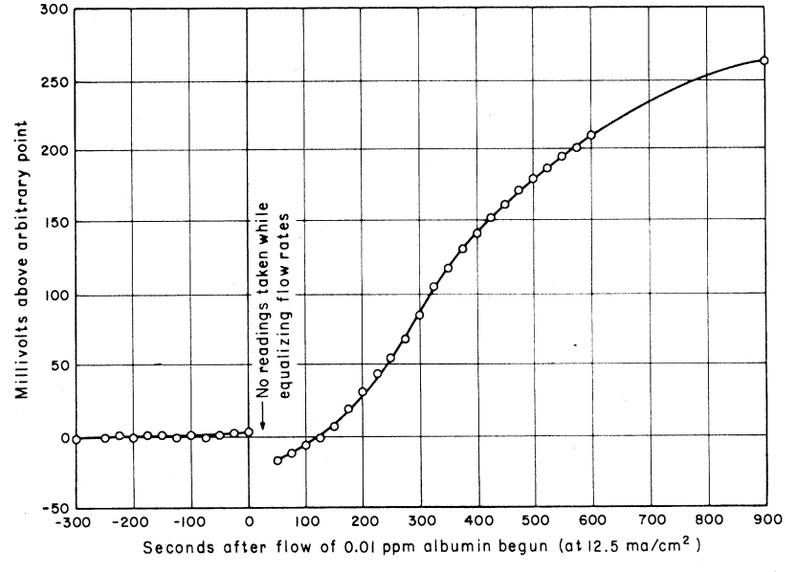


Fig. 1 (left). Overvoltage as a function of current density in 0.1*N* H_2SO_4 solutions. *A*, Range of variation in control runs with unstirred and flowing cells. Additions of ethanolamine and tetramethylammonium bromide at $10^{-3}M$ also were within this range. *B*, Di-*n*-heptylamine, $2 \times 15^{-7}M$. *C*, Dodecylbenzyldimethylammonium chloride, $10^{-8}M$. *D*, Same, $10^{-7}M$. *E*, Egg albumin, 10^{-8} eq/liter. The dotted line represents the egg albumin curve, assuming its slope to be similar to the slopes of the other curves. Fig. 2 (right). Change in overvoltage as a function of time when egg albumin at 0.01 ppm is added to the continuously flowing cell. The break in the curve occurs during switching of reservoirs and adjustment of flow rate. The rate of change is greatest at 330 seconds; at 900 seconds it still exceeds 10 mv/min.

according to Conway *et al.* (*8*), there is a "transition region" at a distance roughly between 5 and 25 Å from the electrode.

The effect of poisons of low molecular weight on electrode reactions has been interpreted largely along the lines of adsorption blocking of sites (*2*, p. 461; *9*). If we apply this concept to the present work, it is easy to show that free energies of adsorption which correspond to about one-tenth coverage of the electrode are not much (about 10 kcal/mole) higher than those which have been measured for smaller organic molecules (*10*).

For di-*n*-heptylamine and DBDA, the slopes of the curves, η plotted against i (Fig. 1), are about the same as the slope of the "control" curve at appreciable current densities. Hence, their effect can be accounted for entirely by site blocking.

However, the large change of η with i caused by the trace of albumin (Fig. 1) cannot be explained entirely by the blockage of active sites; this can be shown as follows. Let i_s and i^o_s = the current per unblocked active site in the presence and absence of albumin, respectively

$$i_s = \frac{i}{p} \text{ and } i^o_s = \frac{i^o}{p^o} \qquad (2)$$

Here, i and i^o are the current densities, and p and p^o are the numbers of unblocked active sites per unit area in the presence and absence of albumin, respectively. The number of blocked sites may be estimated by assuming that the overvoltages are equal when the currents for each active site are equal in the presence and absence of a blocking compound (*11*), in this case, albumin. Or, for $\eta = \eta^o$,

$$i_s = i^o_s, \text{ and } p = p^o + \frac{i}{i^o} \qquad (3)$$

From this relationship, the albumin run would correspond to an (improbable) unblocking of active sites, with increasing current density. Specifically, the active sites in the egg albumin run would increase from about 1/50 to about 1/2 the number of active sites in the absence of albumin, as the current density increases from 0.3 to 6 ma/cm^2.

Further, enough albumin is present at the electrode after 1000 seconds to block all sites effectively (*12*). Yet, according to Fig. 2, the overvoltage was still increasing at the end of this time.

The high molecular weight amines, di-*n*-heptylamine and DBDA, sitting on blocked sites, are big enough to extend somewhat into the transition region of about 25 Å, and can therefore be assumed to lower the dielectric constant of the Stern layer significantly. This results in an increase in η. A higher overvoltage can be expected for quaternary ammonium compounds (curves *C* and *D* of Fig. 1) than for other amines (curves *A* and *B*), since the latter are capable of proton transfer.

This mechanism is, however, insufficient to explain the effect of albumin on overvoltage. The egg albumin molecule in solution is believed to be spherical. If the molecular weight is 45,000 (*13*), it seems reasonable to assume a diameter greater than 50 Å; if denaturation has occurred, the most probable structure is 3 to 5 times as long (*13*). This results in a decrease of the dielectric constant and in a depression of hydrogen ion activity in a film perhaps twice as thick as the usual transition region. It is easily shown that, at the end of 15 minutes (Fig. 1), the concentration of albumin reaches nearly 1000 ppm in the 50-Å thick layer, compared with 0.01 ppm in the bulk phase (*14*). At this concentration significant disturbance of the electrolyte can be expected. As a result, an additional dilute electrolyte film of lowered dielectric constant appears between the 25-Å transition region and the usual polarization layer.

The large potential due to the albumin thus reflects not only the transfer (discharge) potential in the Helmholtz layer but also the combined effect of an increased zeta potential and of an activity potential in the extended transition region.

Comparison of the shapes of the albumin curve and the control curve (no organic contaminant) of Fig. 1 shows that the slope of the albumin curve is significantly greater than that of the control curve, in contrast with the curves for di-*n*-heptylamine and DBDA. The dotted (unlabeled) line in Fig. 1 is drawn roughly parallel to the shaded control area, and the area between the dotted line and experimental curve *E* gives an estimate of the contribution to the total measured overvoltage of the extended transition film. We attribute the significant excess overvoltage caused by the high molecular weight trace of albumin not only to the discharge process itself but also to the change in hydrogen ion activity in the extended transition region in which the transport number of the hydrogen ion changes.

If it is confirmed that a voltage due to the change in film activity is a measure of poisoning at an interface at which activities change, a new mechanism contributing to the understanding of poisoning by macromolecules may have been uncovered.

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12. Egg albumin has a molecular weight of about 44,000 and an equivalent weight of about 1100. Its mobility at *p*H 1 (0.1*N* H_2SO_4) is of the order of 10^{-4} cm/sec; that of H^+ is about 30×10^{-4} cm/sec. Hence, the fraction of the current carrying albumin from bulk to electrode is about 0.33×10^{-8}. At 12.5 ma/cm^2, the total current is about 7.5×10^{16} ion/cm^2 sec. After 1000 seconds 0.6×10^{10}/cm^2 molecules of albumin had "arrived" at the cathode. According to F. Nagy, G. Horanyi, G. Vertes [*Acta Chim. Hung.* **34**, 35 (1962)] the number of active sites on platinized platinum is 0.6 to 1.3×10^{10} cm^{-1}. With only a light platinization, it seems likely that between one-half and all the active sites were "blocked."
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14. Assume a surface layer Å thick. For each square centimeter the volume is 50×10^{-8} ml. If 6×10^9 molecules of albumin are at the surface (*12*), for a molecular weight of 45,000 there are 4.5×10^{-10}, or a concentration of about 900 ppm.
15. We thank J. O'M. Bockris for helpful discussions and suggestions, and Paul Goldberg for critical review of the manuscript. The work was supported by U.S. Army Chemical Corps contract DA 18-108-AMC-29(A).

23 June 1964