



## MEMORY EFFECT OF pH GLASS ELECTRODES IN EMULSIONS

SREČKO OMAN

Department of Chemistry, University of Ljubljana, 61000 Ljubljana, Slovenia

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**Summary**—In the pH measurements of very viscous w/o emulsions, having a high electrical resistance, the “memory effect” of glass membrane is observed. Its dependencies on type of glass and on pretreatment conditions of electrode membrane, and its relation to the gel layer properties are presented. The results complement the findings of other authors.

Properties of the surface layer of pH glass membrane, where the mechanism of potential forming processes is not yet completely clear, were thoroughly investigated in the 1970s. Most of the results were summarized in a monograph on membrane electrodes.<sup>1</sup> There, all statements refer to experiments carried out in aqueous and non-aqueous liquids of relatively low viscosity and common diffusion. Essentially different are the conditions in pH measurements of semi-solid w/o emulsions or creams, which have a significantly higher viscosity, low diffusion and a very high electrical resistance. Therefore, an indirect extraction method is used nowadays for estimation of their pH values. With a modified combination glass electrode<sup>2</sup> we have set up new experimental conditions for pH measurement in these media and we have obtained directly pH values (according to the operational definition of the measured pH!) of an acceptable precision.

In the presented work the behavior of pH glass electrodes in semi-solid w/o emulsions was studied. Agreement with the findings of the above mentioned investigations has been found. In addition, an uncommon and noteworthy response of the glass membrane has been observed and the research of this response should contribute to a further clarification of glass electrode behaviour.

### EXPERIMENTAL

Lanolin–water emulsions are w/o emulsions consisting of a continuous oil phase, throughout which the water is dispersed as globules, mostly containing some emulsifying agent. pH

values of these lanolin–water emulsions, prepared in laboratory, and of some commercial creams (Solea, Oaza, Baby cream) were measured at room temperature with the pH meter 26, Radiometer, using the common technique of measurement. A Servogor RE 646 (Goertz) recorder was used to record the prolonged measurements. Electrical resistivities of samples were determined with the aid of a special conductance cell (Fig. 1A) and a megaohmmeter MA 2073, Iskra. Combination glass electrodes with a flat membrane of Corning 015 glass or a lithium-silicate glass were used after being modified as described below.

Electrical resistances of samples as measured with the mentioned conductance cell, were in the range of the input resistance of pH-meter ( $R \sim 10^{12} \Omega$ ). Therefore the measurement, applying two separated electrodes is not possible. Accurate measurements would not have been possible if the pH cell resistance had not been reduced to  $R \sim 10^9 \Omega$  with a parallel resistance represented by the hydrated glass surface of the combination electrode stem between the liquid junction and the glass membrane (Fig. 1B). To obtain a defined and reproducible surface on this part of the electrode, the lower part of the electrode was etched for 10 sec in a 5% aqueous hydrofluoric acid. Namely, a similar undefined “surface potential” as assumed on the glass surface of the electrode stem was detected also when emf was measured between two equal saturated calomel electrodes, when they had the liquid junctions a few cm apart on the same glass tube which was immersed in the emulsion (Fig. 1C). The values reached up to 30 mV and

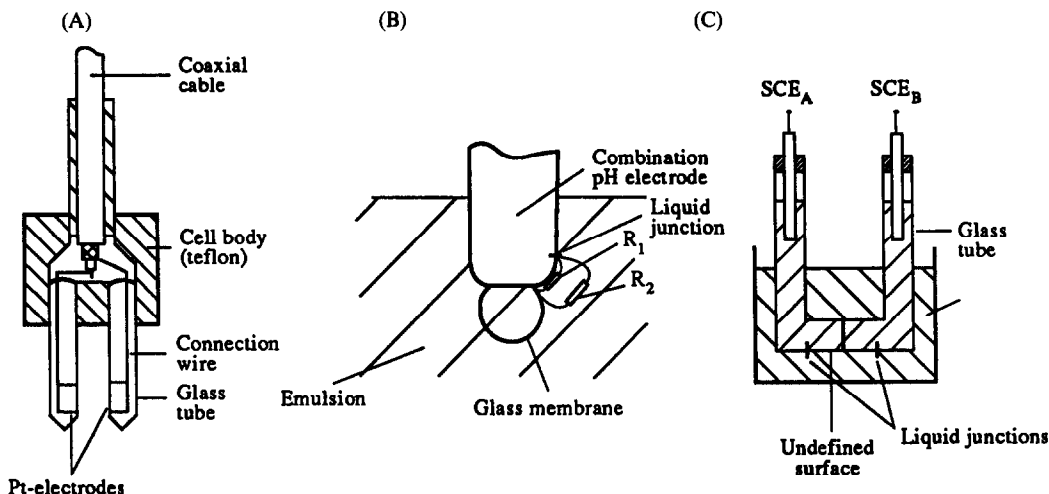


Fig. 1. (A) Conductance cell for measurement of the electrical resistivities of w/o emulsions. (B) A model of location of the parallel resistance  $R_1$  ( $10^9 \Omega$ ) of the hydrated glass surface and of the resistance  $R_2$  ( $10^{12} \Omega$ ) of the bulk of emulsion between the liquid junction and the glass membrane. (C) Construction of the cell composed of two SCE-s on one glass tube, used for measurement of the "surface potential" between the liquid junctions on the undefined surface of glass before etching.

beyond. They were caused by the treatment of the glass in the fire.

While etching the combination glass electrode, the gel layer of the glass membrane was removed as well, and its pH response was changed. The etched membrane was left in water for hydration until a steady state was reached in the gel layer thickness.

During the hydration process of the electrode membrane this electrode was used for several pH measurements of one type of cream (Solea). These measurements showed that the Corning 015 glass membrane needed about three weeks and the lithium-silicate glass membrane about two weeks for the gel layer to reach a steady state. Before each pH measurement the electrode was conditioned: thoroughly cleaned, it was standardized and put in the bidistilled water of a temperature of  $50^\circ\text{C}$  and left to cool to room temperature. During this time (about 30 min) nitrogen gas was bubbled through the water.

Standardization and hydration processes were repeated when necessary.

The ceramic plug of the combination electrode was covered with a piece of filter paper which was fastened with a plastic collar on the electrode stem and soaked with sat. KCl solution. In this way modified liquid junction was found to be the most appropriate for pH measurements in such emulsions. If not pre-treated in the prescribed manner, the electrode (with the gel layer in a steady state) showed a "memory effect". In fact, a significant influence

of the pH value of the preceding sample on the pH reading of the measured emulsion sample was observed. This effect is known in pH measurements of liquids,<sup>3,4</sup> but it is less significant and only transitory. To study this effect in detail the electrodes were not conditioned according to the previously proposed procedure. Instead, they were kept in various (buffer) solutions for a defined time. Then they were rinsed with distilled water, wiped with soft paper and applied for pH measurements of a selected w/o cream (Solea).

## RESULTS

pH readings of w/o cream (Solea), measured during the hydration of a newly etched Corning

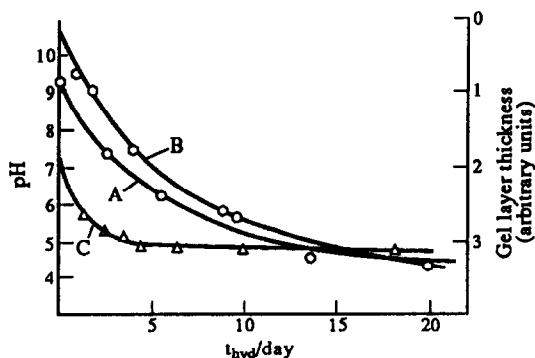


Fig. 2. Dependence of pH readings of commercial cream "Solea" on hydration time after etching for Corning 015 glass (A) and for Li-Ba-silicate glass (C). Curve B—gel layer thickness in dependence on hydration time for Corning 015 glass.<sup>6</sup>

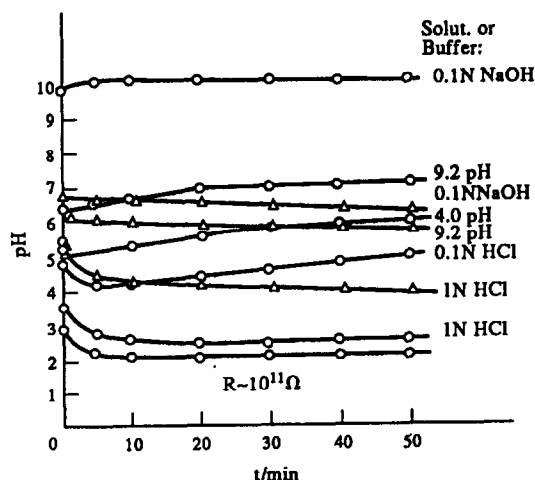


Fig. 3. Time dependence of pH readings obtained with Corning 015 (○) and Li-Ba-silicate (△) glass membrane, pretreated for 15 min in the indicated solutions, while immersed in w/o emulsion, having electrical resistance  $R \sim 10^{11} \Omega$ .

015 glass membrane, were shown elsewhere.<sup>2</sup> The obtained pH values diminished with the time of progressive hydration (Fig. 2). pH readings changed almost proportionally to the increasing gel layer thickness of the membrane.<sup>5</sup>

The etched membrane of lithium-silicate glass showed analogous changing of pH responses, but a shorter time for the complete hydration. Besides, a lower thickness of the steady state gel layer was obtained which is in accordance with other studies.<sup>6,7,8</sup>

In spite of the short (about 30 min) conditioning period of the membrane before each measurement during the hydration of the electrode, different pH readings, proportional to the achieved gel layer thickness, were obtained for the same sample.

From this it can be concluded that, contrary to pH measurement in liquids, the pH measurement in creams requires a steady state of the gel layer thickness in order to obtain repeatable results.

In Fig. 3 the memory effect of Corning 015 glass membrane and of lithium-silicate glass membrane, pretreated in different solutions, is shown.

The memory effect of Corning 015 glass membrane was measured for analogous comparison with other creams (Oaza, Baby cream) and with two o/w emulsions, one containing about 50% and the other 25% of water, both having the electrical resistance  $R < 1 M\Omega$ . Consistency of o/w emulsion samples was the same as that of

the measured w/o emulsions, yet their memory effect was smaller.

## DISCUSSION

While measuring pH of very viscous emulsions the two way diffusion at the glass electrode interface is hindered. The response of glass electrodes is changed. From the curves in Fig. 2 chemical durability of the membrane glasses can be estimated as efficiently as with the more complicated method of electrical resistance measurement.<sup>5</sup>

Figure 3 shows that the "memory effect" of the glass with greater chemical durability is smaller than that of the "soft" Corning 015 glass. Such significant "memory effects" of glass membrane have not yet been found in literature.

Quick changes of emf that occur in the moment of contact of the electrode with the sample could be due to the changes on the outer surface of the membrane double layer.<sup>9</sup> Other changes that follow slowly are presumably due to processes in the inner gel layer.

If "the electrode potential" was generated at the interface sample/gel layer,<sup>10</sup> and if the membrane pretreatment affected only a thin film on the gel layer surface, the potential would reach its final value at the moment when the membrane gets in contact with the sample. Since this is not the case, the influence of pretreatment in liquids must reach deeper into the gel layer. This is in accordance with the concept of operative mechanism of glass electrodes suggested by other authors.<sup>4,11,12,13</sup> In liquid samples two way inter-diffusion accelerates the attainment of equilibrium potential. Very viscous w/o emulsion with special water dispersion, however, hinders the ion diffusion across the interface in both directions, and the same differently conditioned glass membrane can show, depending on the type, up to 7 pH units different pH readings for the same sample even 1 hr or more after the insertion of electrode in the sample (Fig. 3). Another evidence of the gel layer effect on accountability for the mentioned pH deviations is the different behavior of membranes made from Corning glass 015 if compared to those from chemically more resistant (Li-Ba-silicate) glass.

It is interesting to observe that treatment of the membrane in salt solution of NaCl,  $K_2SO_4$  and  $CaCl_2$ , all having nearly the same pH, also exerts a smaller influence inside the gel layer.

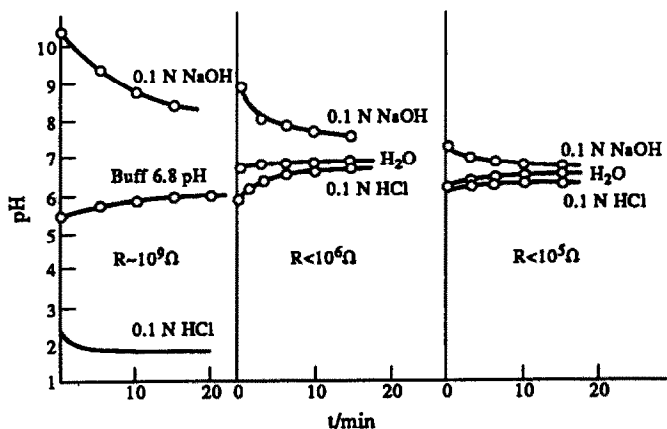


Fig. 4. Time dependence of pH readings obtained with Corning 015 glass membrane, pretreated in solutions, while immersed in an w/o emulsion ( $R \sim 10^9 \Omega$ ) and in two o/w emulsions ( $R < 10^6 \Omega$  and  $R < 10^5 \Omega$ ) containing added water.

In o/w emulsions the "memory effect" is much smaller than in w/o emulsions even though they have a similar consistency. This supports the conclusion that the presence of the free water phase, which enables a better diffusion, is decisive for the speed of potential changes in glass membranes, Fig. 4.

Figure 5 presents the time dependence of electrode response on successive conditioning in the same solution. The sequence of membrane pretreating process influences the response of the electrode immediately after etching and after multiple conditioning in 0.1M HCl. The curve configurations are probably due to the for-

mation of the gel layer (see Fig. 2) and to the diffusion of protons in it (see Fig. 3).

From the presented work it could be concluded, that the formation of the inner part of the gel layer is in a special way the cause for the electrode potential response, and not only the sample contacting surface of the membrane gel layer. It is also obvious that the interdiffusion of ions at the membrane surface is dependent on viscosity of contacting samples. This phenomenon is of great importance for the response time of the electrode and for the pH reading. The results obtained are in accordance with the recent concepts of the mechanism of potential formation on the glass membrane.

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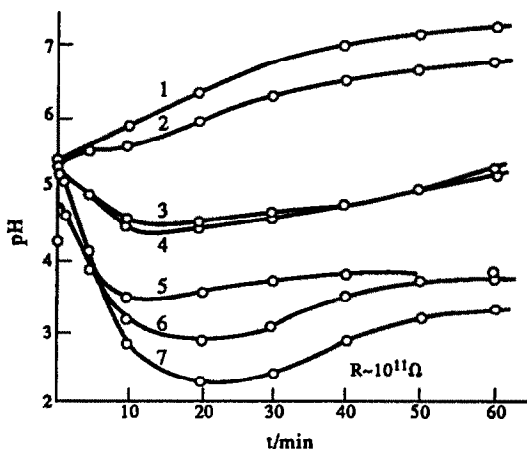


Fig. 5. Time dependence of pH readings obtained with etched Corning 015 glass membrane immersed in w/o emulsion ( $R \sim 10^{11} \Omega$ ) (curve 1) and after multiple sequent conditioning in 0.1M HCl (curves 2 to 7). Influences of the gel layer growth and of membrane "memory effect" on the shape of curves are evident.

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