# Chemical Durability of Some Lead Borate Glasses in Different Aqueous Solutions

Z. A. EL-HADI

*Department of Chemistry, University College for Girls, Ain-Shams University, Heliopolis, Cairo, Egypt*

Received 14 March 1994

The effect of hydrochloric acid and sodium hydroxide solutions on some lead borate glasses containing high proportions of lead oxide was investigated to study the chemical durability of these glasses in different aqueous media. Different factors were studied such as the glass composition, concentration of the aqueous solution, temperature, and time of immersion. The change in the value of the mass loss ($\delta$/(g cm$^{-2}$)) with the change in the glass composition was found to be due to the change in the corrosion rate. In the case of increasing the concentration of the immersion solution, the increase in the mass loss can be attributed to the pH value. The results obtained from the immersion condition were also explained.

Glass is distinguished, besides other properties, by its great resistance with respect to most chemicals at usual temperatures. Without this property, the wide range of the glass applications would be unthinkable. The term chemical durability has been used conventionally to express the resistance offered by a glass towards the attack by aqueous solutions and atmospheric agents. There is no absolute or explicit measure of the chemical durability and the different glasses are usually graded relative to one another after subjecting them to similar experimental conditions.

The interactions between a glass and different aqueous solutions generally depend on the nature of the glass itself, the chemical composition of the glass is of prime importance in this respect while the interface between the glass and the aqueous solution is of no less importance [1].

Chemical attack mechanisms can be visualized in two ways, leaching or the selective removal of the soluble glass constituents and etching which involves the hydration followed by the total dissolution. In fact, any particular reaction will usually involve both of these mechanisms, one or the other predominating [2]. Several theories have been advanced for understanding the glass corrosion mechanisms such as those discussed by *Holland* [3], *Das* [4], *Budd* and *Frackiewicz* [5], and *Douglas* and *El-Shamy* [6].

Strong alkali hydroxides are the most corrosive solutions to the glass after hydrofluoric acid; the rate of attack by the alkali ion is generally linear with time and also it may be influenced by the presence of other ions [2]. On the other hand, acids react much more slowly with the glass than do the strong alkali hydroxides and the rate of attack in the ideal case is proportional to the square root of the time [2].

In the present work, the effect of hydrochloric acid and sodium hydroxide solutions on some lead borate glasses containing high proportions of lead oxide has been studied with the aim to interpret the reation mechanism of these glasses with the various aqueous solutions.

## EXPERIMENTAL

Binary lead borate glasses of variable lead oxide to boron oxide ratios were prepared. Details of the glass compositions studied are given in Table 1. Boron oxide was introduced in the form of boric acid and lead oxide was introduced in the form of $Ph_3O_4$ and was sieved to get rid of the coarse particles. Each melt was made in Pt—2 % Rh crucibles in an electrically heated furnace at 1100 °C for 4 h. The glass melt was poured and cast into a rectangular slab on a heated steel plate. The glass samples were then annealed. Grinding and polishing were carried out in the usual way but with the minimum amount of water and in the final stage of polishing, paraffin oil was used.

**Table 1.** Compositions of Lead Borate Glasses Studied

| Samples | $w_i$/% | |
|---|---|---|
| | PbO | $B_2O_3$ |
| *1* | 55 | 45 |
| *2* | 65 | 35 |
| *3* | 75 | 25 |
| *4* | 80 | 20 |
| *5* | 85 | 15 |
| *6* | 90 | 10 |

The glasses under investigation were immersed in 0.1 M-HCl solution at 27 °C for 2 h. Also different factors such as the concentration of the acid solution, temperature of the immersion solution, and the immersion time were studied. The effect of sodium hydroxide solution was also studied in the same way.

The mass loss ($\delta/(g\ cm^{-2})$) was calculated for all the glasses studied.

## RESULTS

The experimental results obtained are summarized as follows.

### Effect of the Glass Composition

Some lead borate glasses of the base composition ($w_i$) ranging from 55 % PbO and 45 % $B_2O_3$ to 90 % PbO and 10 % $B_2O_3$ (Table 1) were immersed in 0.1 M-HCl. Another group of lead borate glasses of the same compositions were immersed in 0.1 M-NaOH. The immersion temperature was 27 °C and the time of immersion was 2 h, in the above two cases. The variation of the mass loss with the glass composition is shown in Fig. 1*a* and *b* for the above immersion solutions, respectively. From these figures it can be seen that the mass loss ($\delta/(g\ cm^{-2})$) increases with increasing the lead oxide content.

### Effect of the Immersion Solution Concentration

A glass of the base composition ($w_i$) 80 % PbO and 20 % $B_2O_3$ was immersed in HCl solution of different concentrations ranging from 0.1 to 5 mol $dm^{-3}$. Another glass of the same composition was immersed in NaOH solution of the above different concentrations. The immersion temperature was 27 °C for 2 h, in the above two cases. The mass loss for each glass sample was calculated at each solution concentration. The experimental results obtained are shown in Fig. 2*a* and *b* for HCl and NaOH as the immersion solutions, respectively, from which it can be seen that the mass loss increases with increasing the concentration of the immersion solution.

### Effect of the Temperature of the Immersion Solution

A glass of the base composition ($w_i$) 80 % PbO and 20 % $B_2O_3$ was immersed in 0.1 M-HCl for 2 h at different temperatures ranging from 27 °C to 100 °C. Another glass of the same composition was immersed in 0.1 M-NaOH, using the above immersion condition. The mass loss for each glass was calculated at each temperature of the immersion solution. The results obtained revealed that the mass loss increases with the increase of the immersion temperature as shown in Fig. 3*a* and *b* for HCl and NaOH solution, respectively.

### Effect of the Immersion Time

A glass of the same composition was immersed in 0.1 M-HCl at 27 °C for different periods of time ranging from 120 min to 720 min. Another glass of the same composition was immersed in 0.1 M-NaOH, using the above immersion condition. The mass loss for each

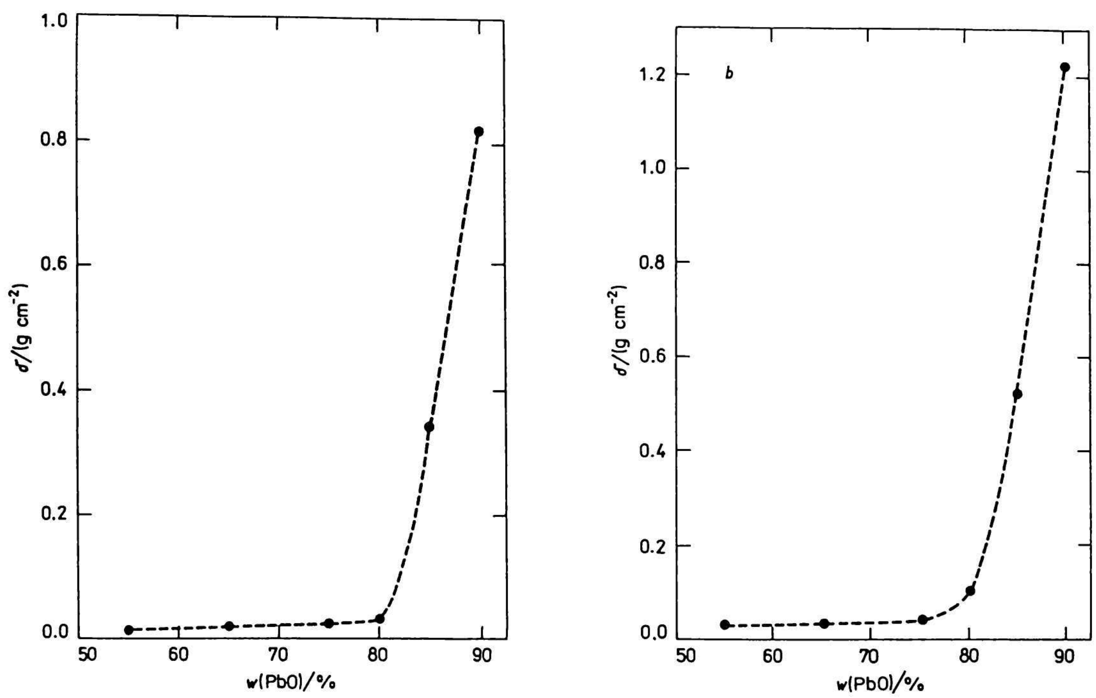



**Fig. 1.** Solubility of lead borate glasses in 0.1 M-HCl (*a*) and 0.1 M-NaOH (*b*) *vs.* the lead oxide content.

glass was calculated at each immersion time. From the results obtained (Fig. 4*a* and *b*) it can be seen that the mass loss increases with the increase of the immersion time for HCl and NaOH solution, respectively.

## DISCUSSION

The resistance which the glass offers to the corroding action of different aqueous media is a property of great practical significance and is denoted by the term chemical durability [7]. The interaction between a glass and the different types of aqueous solutions generally depends on the nature of the glass itself [1]. The leaching process, characteristic of the acid attack, is a diffusion-controlled ion-exchange process, involving exchange of the hydrogen ions for the modifier ions present in the glass network interstices [8, 9]. On the other hand, the etching process, characteristic of the alkaline attack, is a first-order reaction and leaves a smooth surface if complete dissolution occurs with no deposition of the reaction products [2].

As for lead oxide, it can be used in different types of commercial glasses, the crystal glass being the most important. The stability diagram of lead oxide in aqueous solutions of different pH values indicates that in the acidic range lead dissolves as $Pb^{2+}$(aq) and

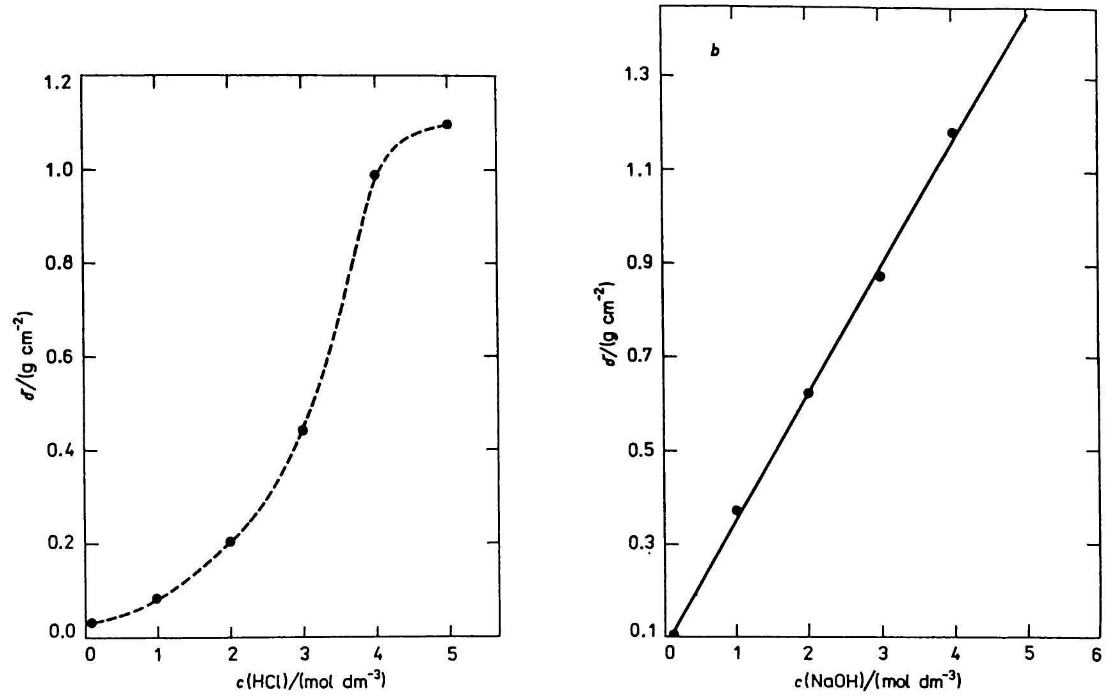



**Fig. 2.** Solubility of a lead borate glass of the base composition ($w_i$) 80 % PbO and 20 % $B_2O_3$ *vs.* the molarity of HCl (*a*) and NaOH (*b*).

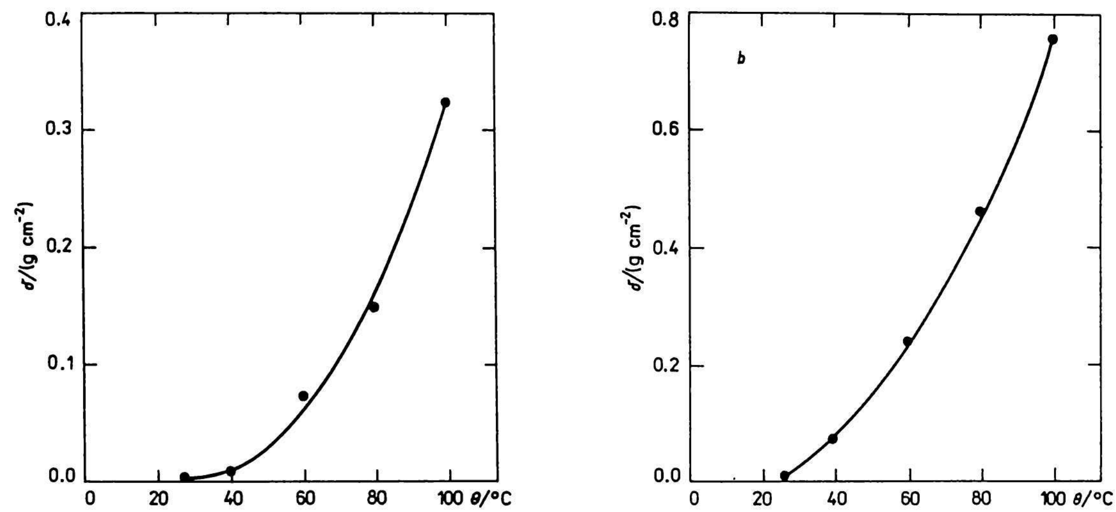
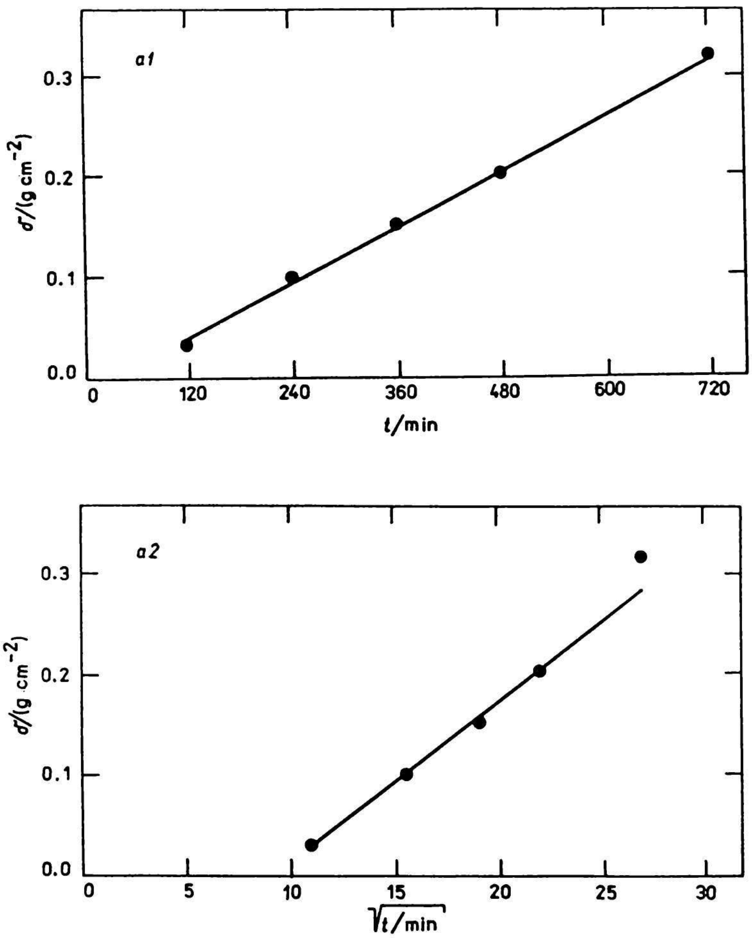



**Fig. 3.** Solubility of a lead borate glass of the base composition ($w_i$) 80 % PbO and 20 % $B_2O_3$ in 0.1 M-HCl (*a*) and 0.1 M-NaOH (*b*) *vs.* the immersion temperature.



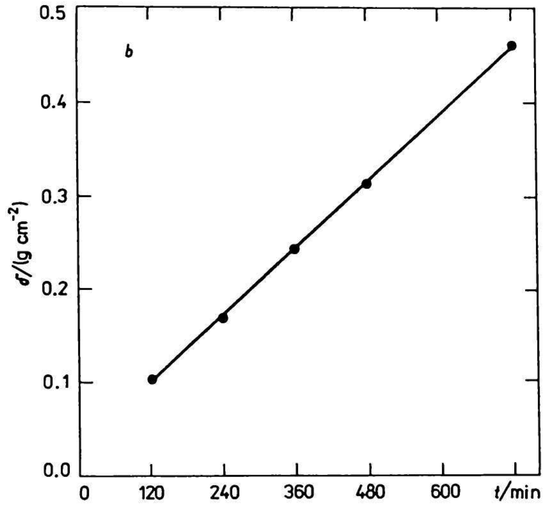
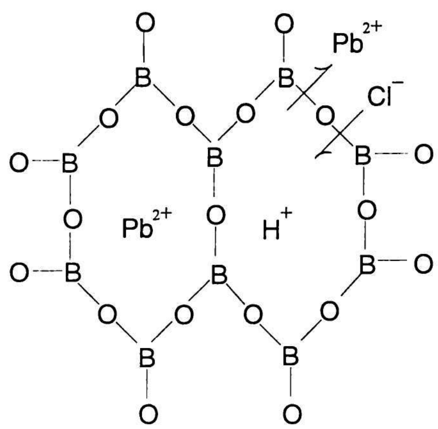



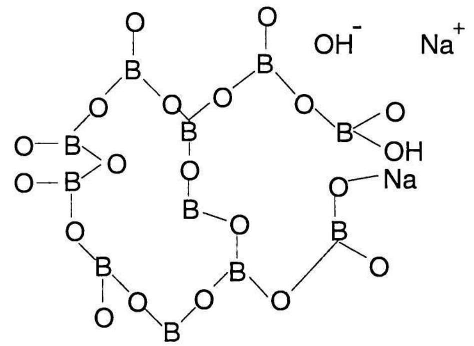

**Fig. 4.** Solubility of a lead borate glass of the base composition ($w_i$) 80 % PbO and 20 % $B_2O_3$ in 0.1 M-HCl (*a*) and 0.1 M-NaOH (*b*) *vs.* the immersion time.

PbOH(aq), the activity of the former being always much greater than that of the latter [7]. In the alkaline range lead forms $HPbO_2$(aq), while boron oxide forms $Na_2B_4O_7$ in aqueous alkaline solutions [1]. According to the above facts, the experimental results obtained can be explained as follows: If the glass of the base composition ($w_i$) 55 % PbO and 45 % $B_2O_3$ is immersed in 0.1 M-HCl, a diffusion-controlled ion-exchange process can take place; it can be represented schematically as follows [2]



Leaching of the glass

On the other hand, when the glass of the above base composition is immersed in 0.1 M-NaOH, the reaction can be represented as follows [2]



Etching of the glass

Accordingly, from the above two reactions, using 0.1 M-HCl or 0.1 M-NaOH as the immersion solution, it can be concluded that the increase in the mass loss with the gradual increase in the lead oxide content (Fig. 1*a* and *b*) can be attributed to the increase in the corrosion rate, *i.e.* the increase in the possibility of leaching or etching process, in the above two cases, respectively [1].

In the case of increasing the concentration of the immersion solution, the increase in the mass loss (Fig. 2*a* and *b*) can be attributed to the increase in the pH value since, generally, the rate of attack on the glass is quite dependent on the pH value of the immersion solution. The different behaviour of the different aqueous solutions can be attributed to their different effect on the glass constituents [2].

The increase in the mass loss with increasing the temperature of the immersion solution (Fig. 3*a* and *b*) may be due to that the extracted amount from the glass, *i.e.* the amount of the glass constituents passing into the aqueous solution in a given period of time increases considerably with temperature [1], while the increase in the mass loss with increasing the immersion time (Fig. 4*a* and *b*) may be attributed to the fact that the glass constituents will have the sufficient time to be released into the immersion solution [2].

The above conclusions can be understood on the basis that in the lead borate glasses the first addition of the lead oxide to boron oxide will cause the $BO_4$ groups to be formed. It is to be expected that with increasing the lead oxide content the $BO_4$ groups will increase progressively and the ratio of $N(BO_4)/N(BO_3)$ groups seems to reach its maximum value in the glass of the approximate composition $w_i$: 75 % PbO and 25 % $B_2O_3$. The increase of the lead oxide content beyond this composition causes a decrease in the $N(BO_4)/N(BO_3)$ ratio [10]. This may be understood when realizing that in these glasses not more than 1/5 of the boron present can be four-coordinated in the glass structure [11, 12]. Furthermore, any additional increase in the lead oxide content beyond this composition causes a disruption on the glassy network and it may be expected that a part of the lead ions exists as $PbO_4$ groups while the remaining lead ions can be housed in the interstices of the glass structure. The two outer electrons of the lead ion are easily repelled by the field of the negative oxygen ion. As a result, the lead ion loses its spherical symmetry and its electron distribution is such that towards the oxygen ions it extends only its 18 electrons of the O-shell, which means that it assumes the electron distribution of much smaller and highly charged lead ions.

## REFERENCES


1. El-Hadi, Z. A., Gammal, M., Ezz El-Din, F. M., and Moustaffa, F. A., *Cent. Glass Ceram. Bull. 32*, 15 (1985).
2. Adams, P. B., *Glass Containers for Ultrapure Solutions.* Chapter 14, pp. 294—327. Corning Glass Works, Corning, New York, 1973.
3. Holland, L., *The Properties of Glass Surfaces.* Chapman and Hall, London, 1964.
4. Das, C. R., *Glass Ind. 50,* 422 (1969).
5. Budd, S. M. and Frackiewicz, J., *Phys. Chem. Glasses 2,* 115 (1961).
6. Douglas, R. W. and El-Shamy, T. M. M., *J. Am. Ceram. Soc. 50,* 1 (1967).
7. Paul, A., *Chemistry of Glasses.* Chapman and Hall, London, 1982.
8. Hutchins, J. R. (III) and Harrington, R. V., *Encyclopaedia of Chemical Technology.* 2nd Edition. Vol. *1,* No. 10 (Kirk and Othmer, Editors), p. 555. Wiley, New York, 1966.
9. Volf, M. B., *Technical Glasses.* Pitman, London, 1961.
10. Warren, B. E., *Chem. Rev. 26,* 237 (1940).
11. Abe, T., *J. Am. Ceram. Soc. 30,* 277 (1947).
12. El-Batal, H. A. and Abbas, A. F., *Trans. Indian Ceram. Soc. 31,* 36 (1972).