CHEMICAL DURABILITY OF SOME LEAD BORATE GLASSES IN DIFFERENT AQUEOUS SOLUTIONS

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ABSTRACT

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 (δ in 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.

INTRODUCTION

Glass is distinguished, among other properties, by its great resistance with respect to almost 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 visualised with two concepts, leaching or the selective removal of the soluble glass constituents and etching which involves the hydrations 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 et al [5] and Douglas et al [6].

Strong alkali hydroxides are the most corrosive solutions to the glass after hydroffluoric acid; the rate of attck 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 containing high proportions of lead oxide has been studied with the aim to interpret the reaction mechanism of these glasses with the various aqueous solutions.

EXPERIMENTAL

Binary lead borate glasses of variable lead oxide to boric oxide ratios were prepared. Dtails of the glass compositions studied are given in Table 1. Boric oxide was introduced in the form of boric acid and lead oxide was introduced in the form of Pb_3O_4 and was sieved to get rid of the course 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.

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

Table 1. Glass Compositions of Lead Borate Glasses Studied

	Glass Composition w_i / %	
	PbO	B_2O_3
1	55	45
2	65	35
3	75	25
4	80	20
5	85	15
6	90	10

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 (δ in g cm^{-2}) was calculated for all the glasses studied.

RESULTS

The experimental results obtained are summarised as follows:

Effect of the Glass Composition

Some lead borate glasses of the base composition ranging from 55 w_i / % PbO, 45 w_i / % B_2O_3 to 90 w_i / % PbO, 10 w_i / % 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, for both group of experiments. The variation of the mass loss with the glass composition is shown in Figs 1 and 2, for the above immersion solutions respectively. From these two figures, it can be seen that the mass loss (δ in g cm^{-1}) increases with increasing the amount of the lead oxide content.

Effect of the Immersion Solution Concentration

A glass of the base composition 80 w_i / % PbO, 20 w_i / % B_2O_3 was immersed in HCl solution of different concentrations ranging from 0.1 M to 5 M. Another glass of the same composition was immersed in Na OH solution of corresponding concentrations. The immersion temperature and period was 27°C and 2 h, respectively, The mass loss for each glass sample was calculated at each solution concentration. The experimental results obtained are shown in Figs. 3 and 4 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 80 w_i / % PbO, 20 w_i / % 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
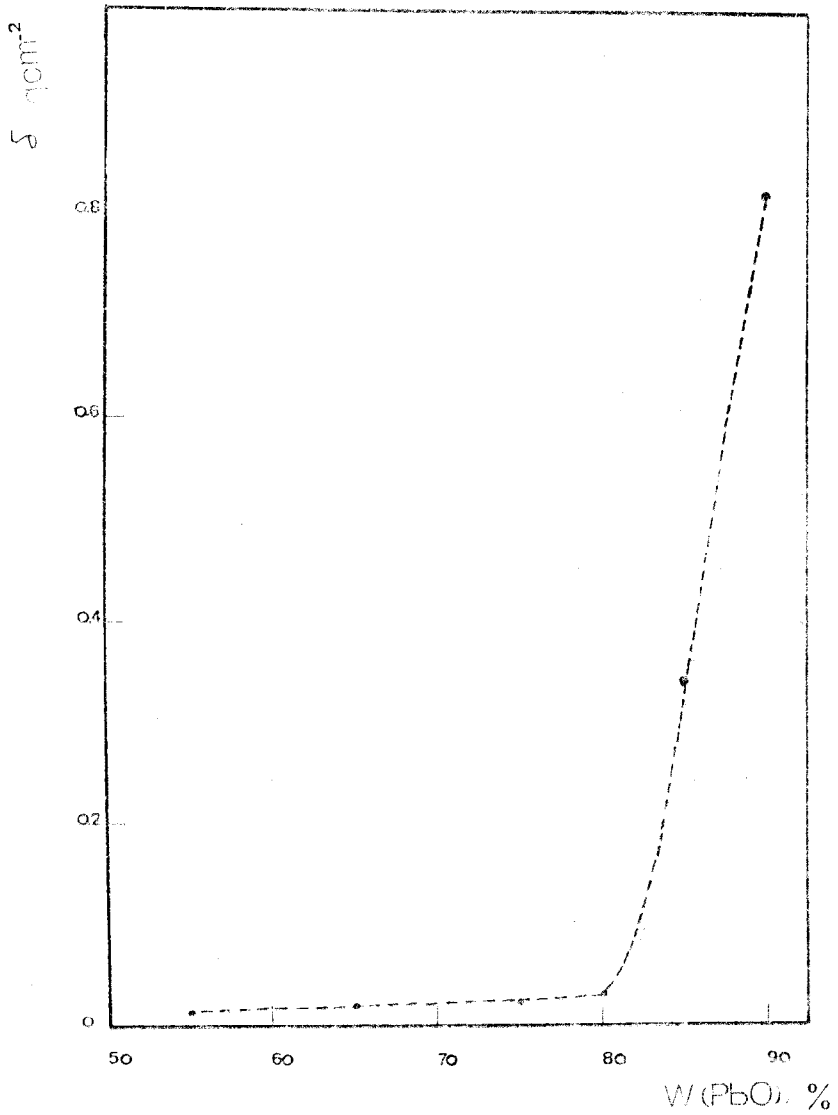
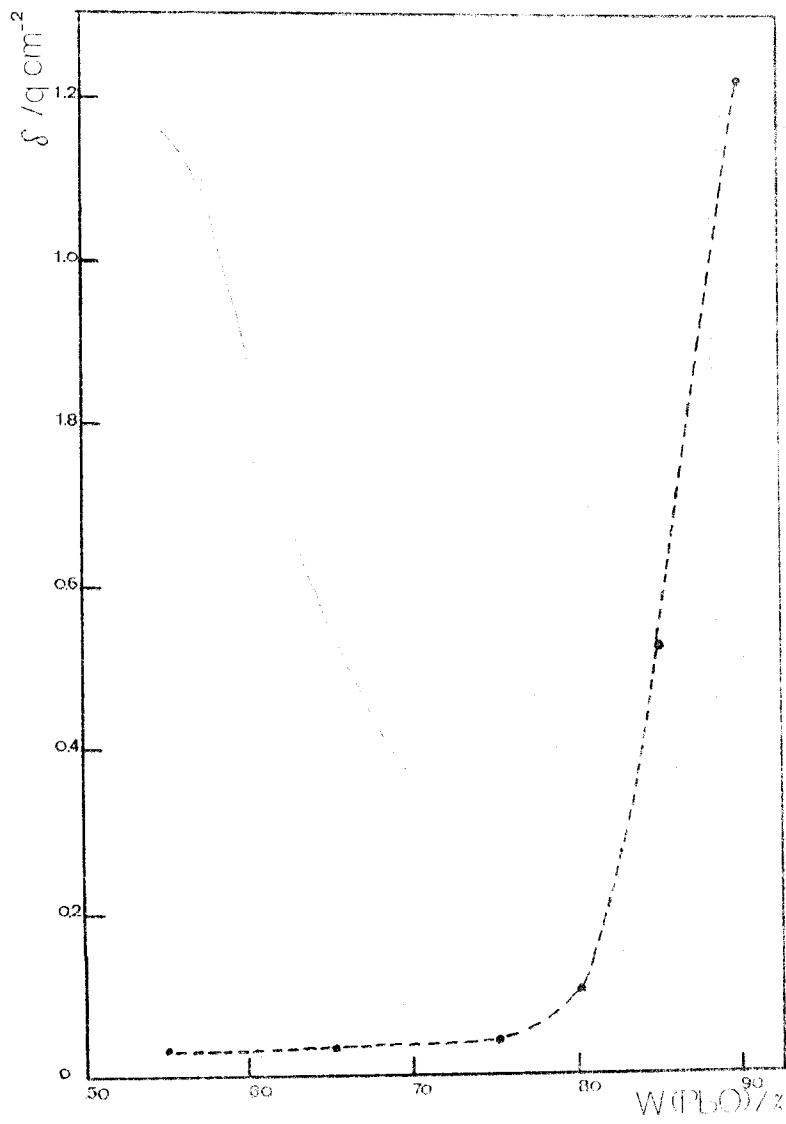Fig. 1. Solubility of lead borate glasses in 0.1 M-HCl vs the lead oxide content.

Fig. 2. Solubility of lead borate glasses in 0.1 M–NaOH vs the lead oxide content.
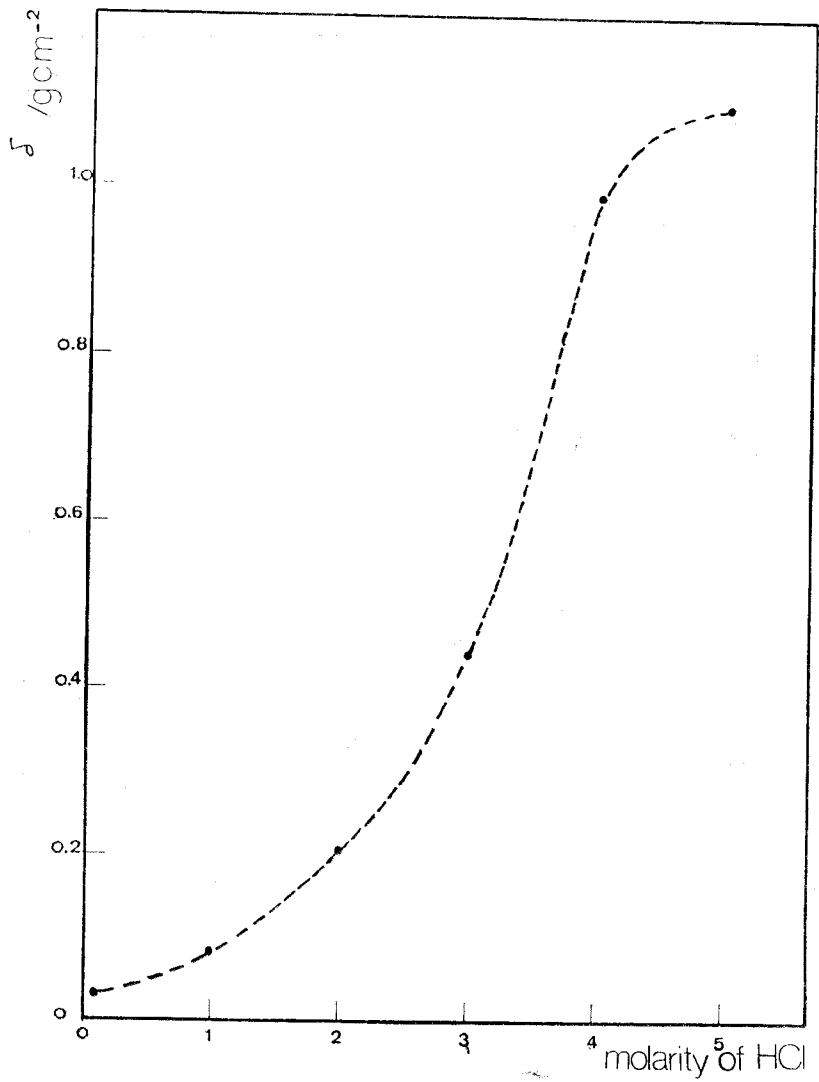
Fig. 3. Solubility of a lead borate glass of the base composition 80 w_i / % PbO, 20 w_i / % B_2O_3 vs the molarity of HCI.
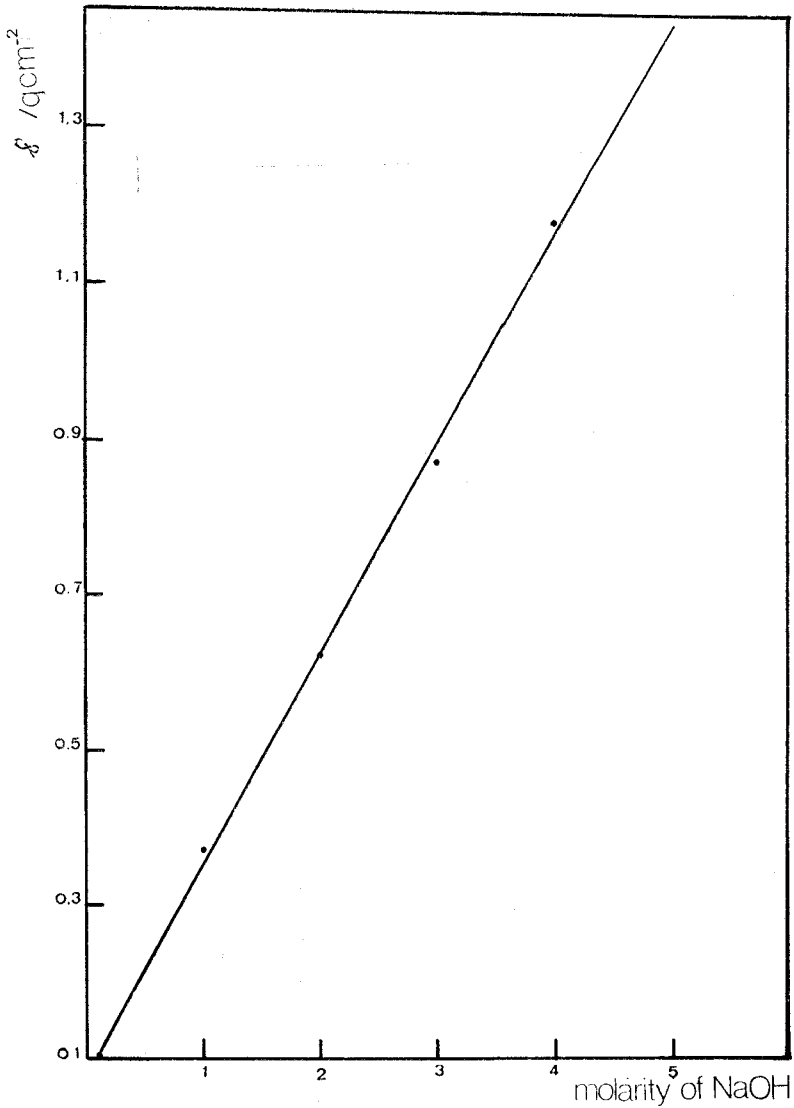
Fig. 4. Solubility of a lead borate glass of the base composition 80 w_i / % PbO, 20 w_i / % B_2O_3 vs the molarity of NaOH.

in 0.1 M NaOH, using the above same 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 Figs 5 and
6 for HCl and NaOH solutions respectively.
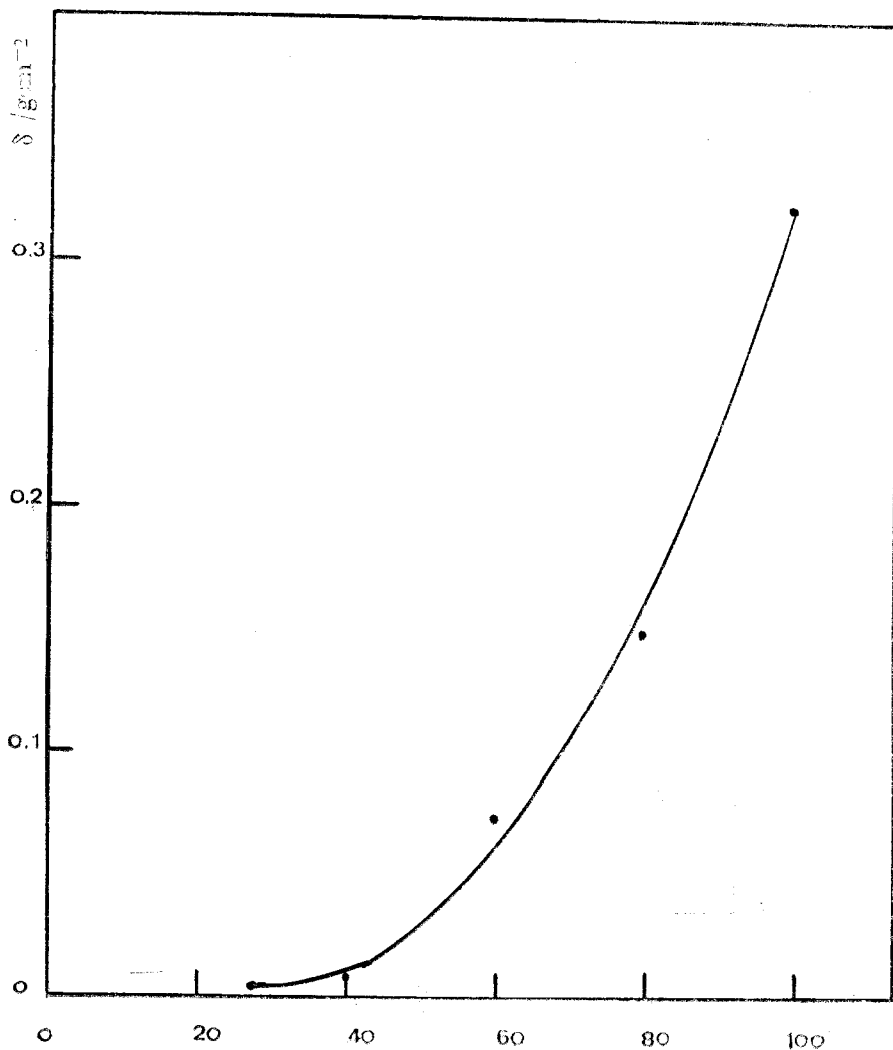
Effect of the Immersion Time

Fig. 5. Solubility of a lead borate glass of the base composition 80 w_i / % PbO, 20 w_i / % B_2O_3
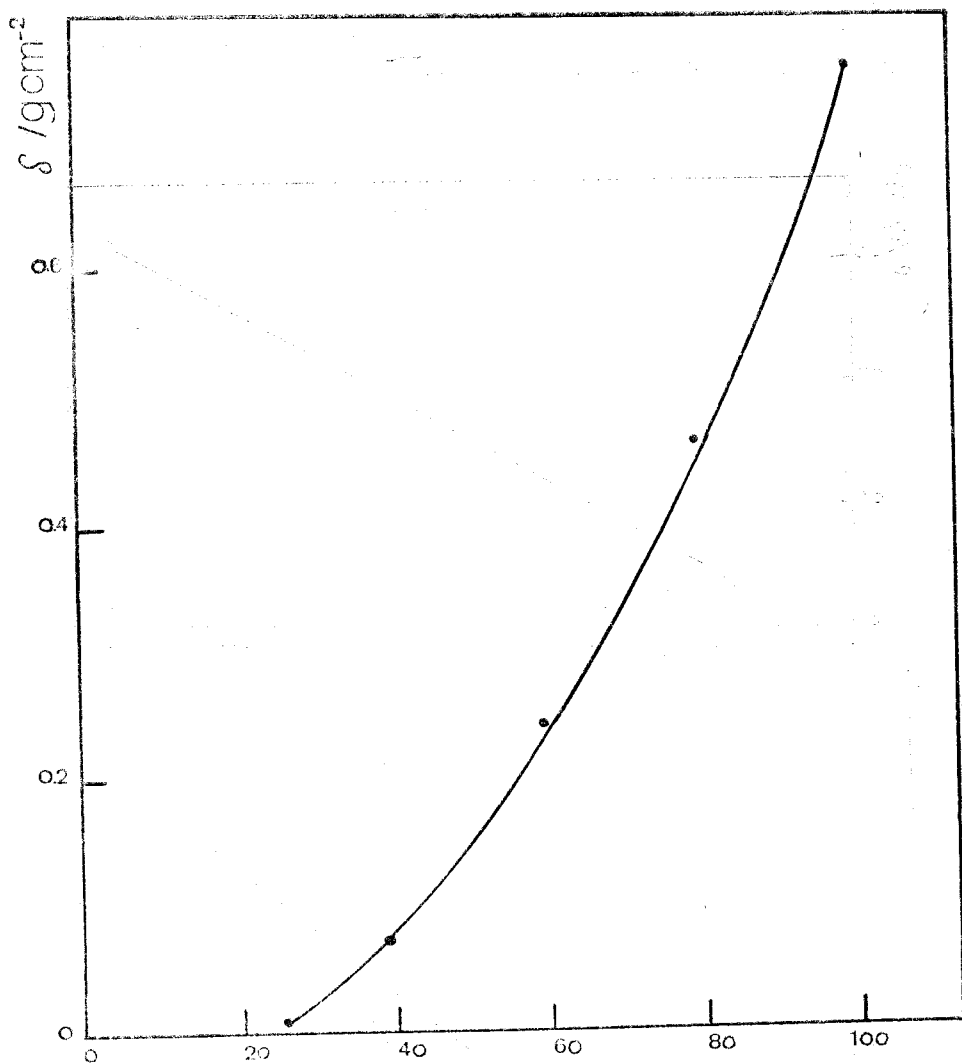in 0.1 M-HCl vs the immersion temperature.

Fig. 6. Solubility of a lead borate glass of the base composition 80 $w_i/\%$ PbO, 20 $w_i/\%$ B_2O_3 in 0.1 M–NaOH vs the immersion temperature.

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 immersion condition. The mass loss for each glass was calculated at

each immersion time. From the results obtained (Figs 7 and 8), it can be
seen that the mass loss increases with the increase of the immersion time
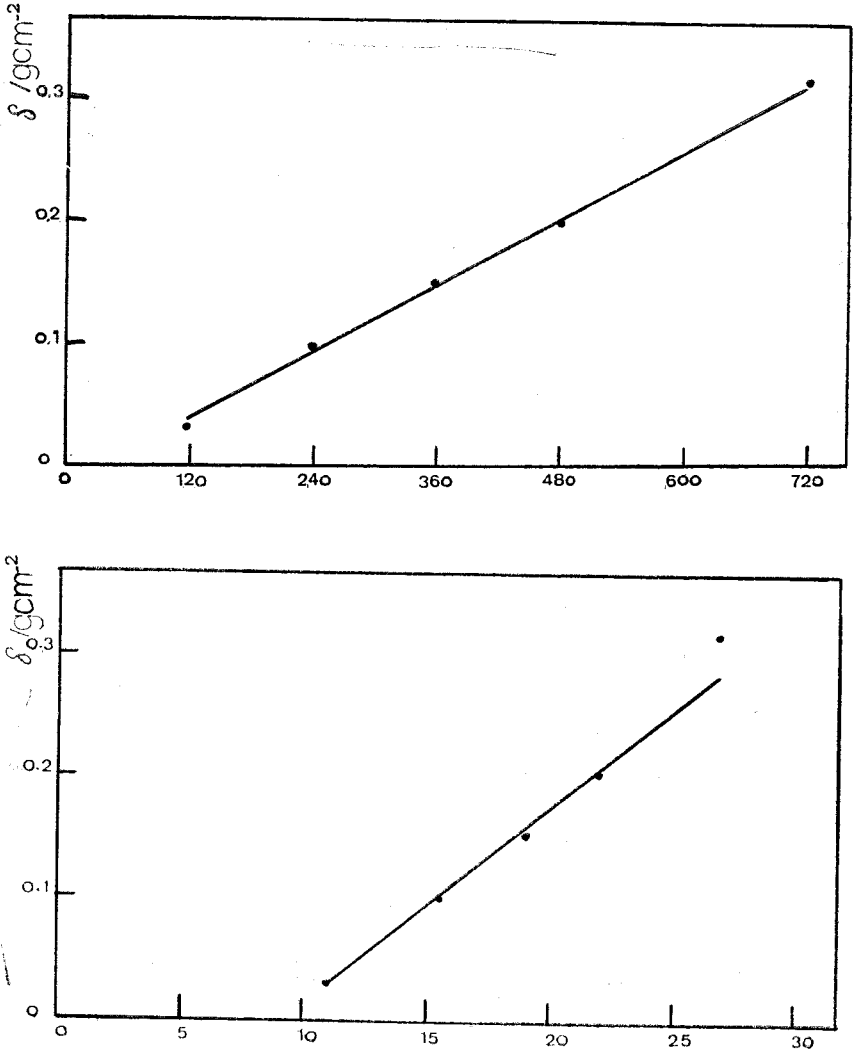for HCl and NaOH solutions respectively.

Fig. 7. Solubility of a lead borate glass of the base composition 80 w_i / % PbO, 20 w_i / % B_2O_3
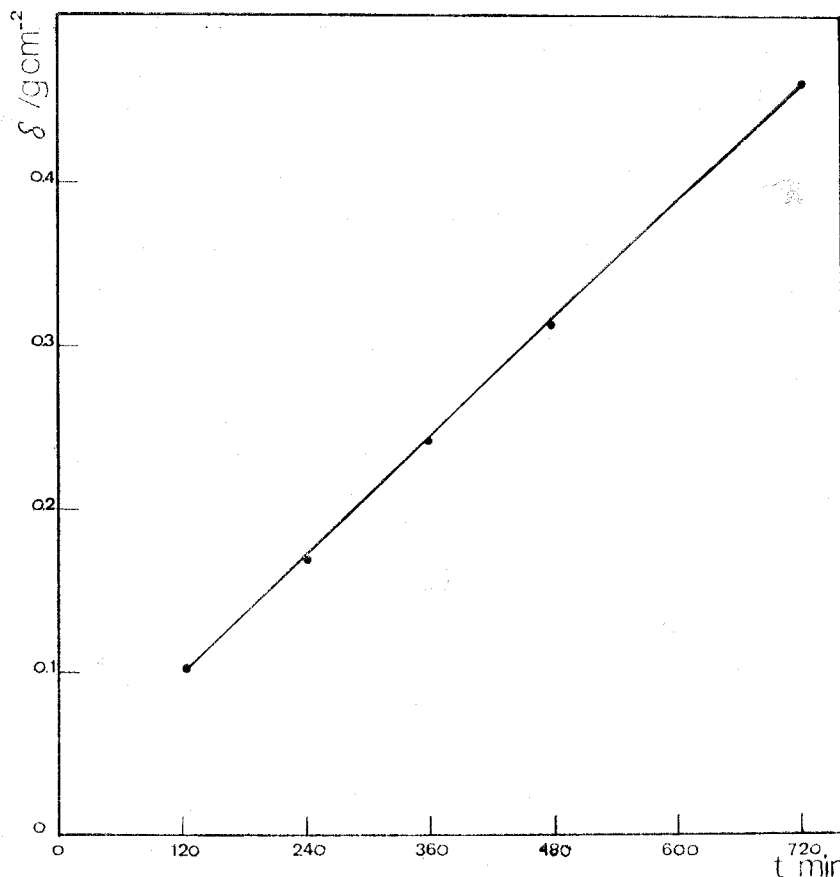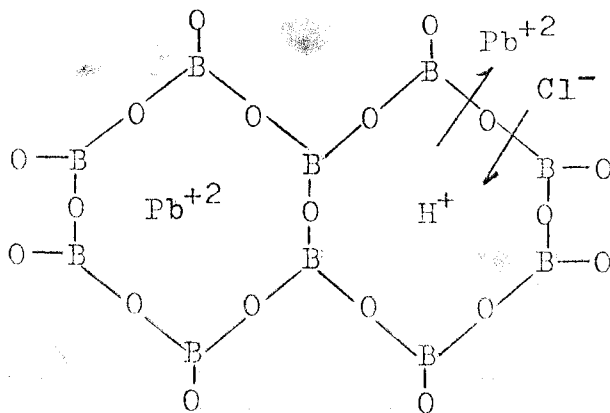in 0.1 M-HCl vs the immersion time.

Fig. 8. Solubility of a lead borate glass of the base composition 80 w_i / % PbO, 20 w_i / % B_2O_3
in 0.1 M-NaOH vs the immersion time.

DISCUSSION

The resistance which the glass offers to the corroding action of dif-
ferent 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 depend
on the nature of the glass itself 1. The leaching process, characteristic
of the acid attack, is a diffusion controlled ion exchange process, invol-
ving exchange of the hydrogen ions for the modefier ions present in the
glass network interstices [8] and [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 depositi-
on of reaction products 2.

With respect to lead oxide, it can be used in different types of com-
mercial glasses, the most impotant being the crystal glass. The stability
diagram of lead oxide in aqueous solutions of different pH values indi-
cates that in acidic range lead dissolves as Pb^{2+} (aq) and PbOH (aq),
the activity of the former being always much greater than that of the
latter [7]. In the alkaline range lead forms $HPb\,O_2$ (aq), while boric
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 55 $w_i/\%$ PbO, 45 $w_i/\%$
B_2O_3 is immersed in 0.1 M HCl, a diffusion controlled ion exchange
process can take place, this process can be represented schematically
as follows [2]:

Leaching of the glass

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

Accordingly, from 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 (Figs
1 and 2) can be attributed to the increase in the corrosion rate, ie, the
increase in the possibility of leaching or etching process, in the above
two states respectively [1].
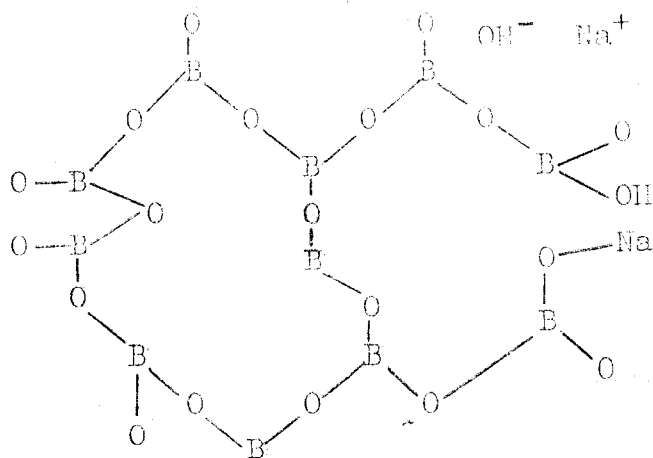
Etching of the glass

In the case of increasing the concentration of the immersion soluti-on, the increase in the mass loss (Figs 3 and 4) 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 constitutents [2].

The increase in the mass loss with increasing the temperature of the immersion solution (Figs 5 and 6) may be due to that the extracted amount from the glass, ie, 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 the inc-reasing the immersion time (Figs 7 and 8) may be attributed to the fact that the glass constitutents 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 boric oxide will cause the BO_4 groups to be formed. It is to be expected that, with inc-reasing the lead oxide content the BO_4 groups will increase progressi-vely and the ratio of BO_4/BO_3 groups seems to reach its maximum va-lue in the glass of the approximate composition 75 $w_i/$ % PbO, 25 $w_i/$ % B_2O_3. The increase of the lead oxide, beyond this composition, cau-ses a decrease in the BO_4/BO_3 ratio [10]. This may be understood

when it is realizee that in these glasses not more than 1 / 5 of the boron present can be four coordinated in the glass structure [11] and [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 [13]. 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 looses 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 and Ceram Bull Vol 32, Nos 1-2, Pages 15-19 (1985).

[2] ADAMS, P.B., Glass Containers For Ultrapure Solutions Corning Glass Works, Corning, New York Chap 14. Pages 294-327 (1973).

[3] HOLLAND, L., The Properties of Glass Surfaces. Chapman and Hall, London (1964).

[4] DAS, C.R., Theoretical Aspects of The Corrosion of Glass. Glass Indust. Vol, 50 Nos 1-21, Pages 422-427 (1969).

[5] BUDD, S.M. and FRACKIEWIEZ, J., The Mechanisms of Chemical Reaction Between Silicate Glass and Attacking Agents. Part 2. Chemical Equilibria at Glass-Solution Interfaces. Phys Chem Glasses Vol 2, No 4, Page 115 (1961).

[6] DOUGLAS, R.W. and EL-SHAMY, T.M.M., Reactions of Glasses With Aqueous Solutions. J. Amer Ceram Soc Vol 50, No 1, Page 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 .Kirk and Othmer Vol 1, No 10, Page 555, Wiley, New York (1966).

[9] VOLF, M.B., Technical Glasses. Pitman, London (1961).

[10] WARREN, B.E., Chem Rev Vol 26, Page 237 (1940).

[11] ABE, T., J Amer Ceram Soc Vol 30, Page 277 (1947).

[12] EL-BATAL, H..A. and ABBAS, A.F., Trans Indian Ceram Soc Vol 31, No 1, Pages 36-38 (1972).