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ALUMINA SURFACES

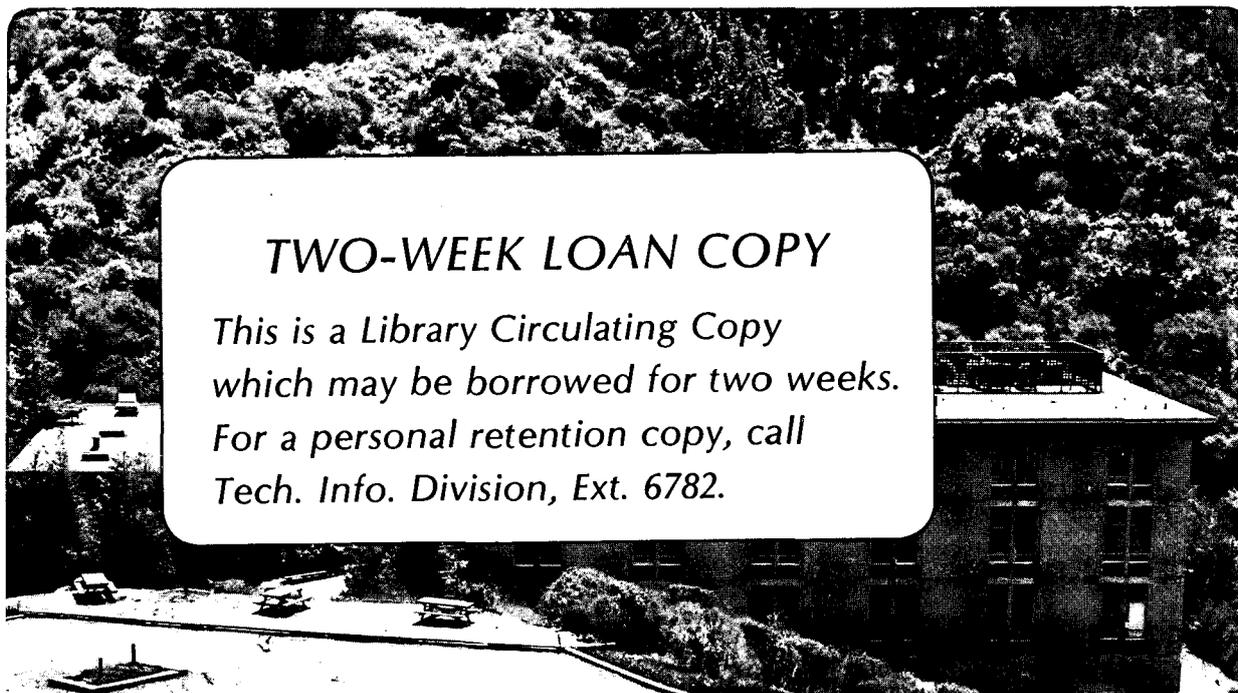
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THE ELECTROPHORETIC BEHAVIOR OF SILICA-BEARING ALUMINA SURFACES

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ABSTRACT

The influence of silica impurity on the electrophoretic behavior of alumina powders with different chemical pretreatments has been studied. Shifts in the isoelectric point (i.e.p.) as a function of pH of suspension, equilibration time and nature of container (pyrex glass or polyethylene) are reported. The results are explained in terms of a coating phenomenon produced through a silica polymerization process.

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## INTRODUCTION

The development of an electric double layer at the oxide/water interface, a fundamental physicochemical phenomenon which takes place when a solid is immersed in water, is of great importance to describe many phenomena, among others, the degree of particle aggregation (flocculation, coagulation) or dispersion. Consequently, the determination of the magnitude and characteristics of this electric double layer is greatly significant and is now a common practice in many fields. Electrokinetic measurements of particles are one of the most well-known techniques for this purpose. The determination of the electrokinetic properties of alumina is of interest to various ceramic processes, such as slip casting and, indirectly, sintering at high temperature, because of their effect on degree of clustering or agglomeration which is critical to these processes. Despite the obvious influence that some contaminants accompanying most solids have on the measurement of the particle electrokinetics, sufficient precautions are not taken in the cleaning and equilibration stages which lead to controversial values in the isoelectric points of common oxides such as alumina. Silica is one of the most common substances that is found associated with commercial alumina; it is, potentially, a very surface active compound when soluble in water. The object of the present investigation is to describe the overall effect that siliceous contaminants have on the surface modification and electrokinetic properties of a typical commercial alumina.

### EXPERIMENTAL

Alcoa "A-14" and "A-12" aluminas with unitary particles ranging from 2-5 $\mu$ m, an average of 3.5 $\mu$ m, were used in this investigation. The spectrographic analysis\* of A-14 in terms of elements is 0.04% Si, 0.01 Ga, 0.03 Fe, 0.02 Ca, 0.001 Mg, 0.02 Na and 0.005 Ti; of A-12, 0.009% Si, 0.01 Ga, 0.05 Fe, 0.01 Ca, 0.001 Mg, 0.2 Na, 0.003 Ti and 0.007 Zn. No grinding aids were used in their preparation.

X-ray diffraction\*\* of the powders showed only  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The powders were submitted to different chemical treatments and stored for different periods of time under triple-distilled water at ~pH 4.5 and ~pH 7 usually in polyethylene bottles and occasionally in pyrex glass containers. The suspensions for electrophoretic measurements were made with 1 g/lit of solid concentration in triple-distilled water.

Electrophoretic mobilities of the alumina particles were determined by means of a Z-meter microelectrophoresis apparatus<sup>†</sup> with a round glass type of cell. The velocity of at least 10 different particles in each direction was measured for each system. The maximum deviation from the average values was not greater than 5 per cent. Measurements were performed at 20  $\pm$  2°C and the ionic strength was kept at 1 x 10<sup>-3</sup> M in NaClO<sub>4</sub>. The pH was adjusted with either NaOH or NaClO<sub>4</sub>. The electrophoretic mobilities were converted into surface potential or Z-potential values according to the procedure of Wiersema et al.<sup>4</sup> who used the correction given by Henry's analysis. These values are critical in

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\* American Spectrographic Lab. Inc., San Francisco, Calif.

\*\* Philips Norelco X-Ray diffractometer with Cu anticathode and with a detectability of ~2%.

† Z-Meter Inc., N. Y.

determining the degree of repulsion between particles which in turn determines the dispersion and aggregation behavior of the powder.

The equation relating the Z-potential to mobility is

$Z = 4\pi\eta\mu/\epsilon(1 + f(ka))$  where  $\eta$  is the viscosity,  $\mu$  - electrophoretic mobility,  $\epsilon$  - dielectric constant of the medium,  $f(ka)$  - a function which controls the relaxation phenomenon,  $k$  - inverse of the double layer thickness, and  $a$  - particle radius which was assumed to be spherical. The  $f(ka)$  varies between zero for small values of  $ka$  and 1.0 for large values of  $ka$ . The equation is only valid for spherical particles and for values of  $ka \gg 1$ , corrections for relaxation phenomena being necessary when  $0.2 < ka < 50$ . For the particle size and solution ionic strength used, the value of  $1/k$  is  $100\text{\AA}$  or  $10^{-2}\mu\text{m}$  which results in a value for  $ka$  of 350.

## RESULTS

The zeta potential vs. pH data obtained were found to be very dependent on the pre-treatment of the alumina sample. Figure 1 shows results obtained for A-14 after a number of treatments. Curve a represents values of Z-potentials obtained after 10 days equilibration of the alumina suspension at pH 4.5 in pyrex glass containers; the isoelectric point was pH 8.7. Curve b shows that with aging of the same alumina powder in glass containers for 24 hours at each of the pH values of measurement, the i.e.p. was found to be pH 7.7. Another sample when stored, again in glass bottles, for 24 days at pH 6.7-7 with intermittent

periods of shaking gave an i.e.p. of ~pH 3.8 (curve d). No significant change in all of these values was obtained after an additional 10 or 15 days of equilibration. Curve c shows an i.e.p. of ~pH 4.8 after the alumina was submitted to the following treatment: 2 g. of powder were leached with concentrated HCl for 4 hours, thoroughly washed with triple-distilled water until no chloride ions were present, and stored at pH ranging from 6.7-7.0 (same as d) for 10 days in pyrex glass containers before the electrophoretic measurements were performed.

Curve e in Fig. 2 shows an i.e.p. of pH 8.9 for A-14 after the following treatment: 2 g. of powder were treated with 200 milliliters of 0.1N HF for one hour under constant shaking at room temperature followed by extensive washing with triple-distilled water. Throughout this process, ultrasound irradiations were applied to disperse the alumina particles with the purpose of improving the efficiency of the cleaning stage. The absence of fluoride ions in the sample solution was checked with the use of a  $F^-$  ion selective electrode. The alumina was then stored under water (at pH 6.9) in polyethylene bottles for 10 days before measurements. Curve f represents a sample treated as in e and aged in polyethylene bottles at pH 3.3. in  $10^{-4}$  M  $Na_2SiO_3$  for 3 days and also for 6 days. The i.e.p. was pH 6.1. Curve g represents values obtained after 16 days equilibration of as-received A-14 suspension at pH ~7 in polyethylene containers. Similar results were observed after 49 days equilibration. The i.e.p. was pH 5.8.

Figure 3 shows additional data on the variation of the i.e.p. with time after different pre-treatments of as-received A-14. Storing in pyrex glass containers at ~pH 7 immediately lowered the i.e.p. reaching

a minimum of ~pH 3.3 after about 16 days of equilibration. On repeating the experiment in polyethylene bottles the i.e.p. decreased less drastically and slower to a value of ~pH 5.8. On the other hand, storing the samples in pyrex glass containers at ~pH 4.5 resulted in no change in the i.e.p. values. HF-treated A-14 aged in polyethylene bottles at ~pH 7 also showed no drop and no change in the i.e.p. As-received A-12 aged under similar conditions also showed essentially no drop in i.e.p.

#### DISCUSSION

The results show that reported differences in electrophoretic mobility and i.e.p. of alumina can be due to the presence of soluble silica which accompanies the powder as an impurity or is introduced by solution from the glass container. Polymerization of the silica and its adsorption is a function of the ageing time and pH of the alumina suspension solution. Silica in the specimen can be removed by HF treatment of the powder, and silica from the containers can be avoided by use of polyethylene bottles.

A number of papers<sup>2-5</sup> have appeared reporting values for the i.e.p. of alumina suspensions ranging from pH 3 to 10. However, the most accepted value is ~pH 9. Impurities are the most probable cause for this difference. Typical surface impurities leading to erratic i.e.p. values are  $\text{SO}_4^{=}$  and  $\text{PO}_4^{=}$  anions, which change the i.e.p. by ~4 pH units towards the acid region. On the same basis silicate anions appearing by dissolution of glass containers used to store the samples may well act similarly. However, no systematic study on the possible role of surface contamination by silica and its soluble byproducts has been reported to date. This impurity is regularly found in commercial aluminas.

Leaching of the solid material with HCl has been a common practice aimed at obtaining a "clean" surface.<sup>2,6</sup> Nevertheless, this process has not succeeded in dissolving all of the impurities and different values have been obtained for alumina after this chemical treatment. The importance of surface contamination on the i.e.p. of most solids by the presence of impurities in the sample or by adsorption of silicate anions from the glass containers is now being considered by others<sup>6,7</sup> as well, and it is being forecast that many of the i.e.p. values reported in the literature will require further evaluation.

The silica present in the alumina powder under favorable conditions in aqueous solution can form soluble species which are "per se" potentially active species as adsorbants. In its polymerization state silica is mainly in the form of an open, random network of partially cross-linked chains which are usually composed of extended polysilicic acid branching out into the medium. These species are thermodynamically unstable and are incapable of condensing into a compact crystalline form (for kinetic reasons) at ordinary temperatures and appropriate pH values.<sup>8</sup> The polymerization rate is a function of pH and according to Iler<sup>3</sup> the reaction has two maxima: one between pH 6 and 8 (which corresponds to one of the storage pH values used in this work) and another between pH 2 and 3.

The silicic and/or polysilicic acid are known to adsorb on quartz.<sup>8</sup> Similarly, they may adsorb on the surface of alumina, thus shifting the i.e.p. towards the more acid region. Similar coating phenomenon has been proposed to explain the high colloidal stability of silica sols (presumably by a protection mechanism) over the entire pH range.<sup>8</sup>

The principal chemical impurity of A-14 is silica, amounting to ~0.1 wt%. On the basis of solubility considerations, it is assumed that this concentration is sufficient to produce "in situ" a coating on the alumina particles, and that this coverage is at certain pH values mainly composed of oligomeric soluble silica species produced in solution; under this condition, the alumina behaves as a silica-like compound. Conversely, when this siliceous impurity is removed from the sample by dissolution with HF, the i.e.p. of the  $\text{Al}_2\text{O}_3$  of ~pH 9 is restored and the value obtained is in agreement with the accepted value given in the literature.

Considering that the adsorbing segment of an oligomeric silica molecule is of the order of  $100 \text{ \AA}^2$  and its approximate molecular weight is 576 based on 6  $\text{Si}(\text{OH})_4$  units,<sup>3</sup> the surface coverage by these species, assuming that the total amount of silica of 0.1% is adsorbed, would amount to  $1.7 \text{ m}^2 \text{ g}^{-1}$ . On the basis of an averaged geometric surface area of  $0.36 \text{ m}^2 \text{ g}^{-1}$  for the A-14 alumina, the silica coating would be of the order of 400% of monolayer. Clearly, the coverage by soluble silica when polymerized by aging at pH 7 is sufficient to produce a change in the electrokinetic behavior of  $\text{Al}_2\text{O}_3$  (Figs. 1 and 3). On the other hand, an alumina containing a similar amount of silica but high specific surface area, such as Linde A which was used in the work of Yopps and Fuerstenau,<sup>4</sup> did not experience this aging process and the reported i.e.p. was pH 9.1. A similar calculation indicates that surface coverage by soluble silica would correspond to a maximum of about a 5% monolayer which is negligible.

In the case of A-12 with an amount of  $\text{SiO}_2$  five times lower than A-14 and a similar specific surface area the effect of aging at ~pH 7 in a polyethylene bottle on the i.e.p. was negligible, as shown in Fig. 3

The greater and faster rate of the lowering of the i.e.p. on ageing at ~pH 7 in glass than in plastic bottles must be attributed to additional contamination by soluble silica from the pyrex glass containers despite the very low solubility of this kind of glass.<sup>9</sup> However, on storing in a glass bottle at pH 4.5 no ageing effect was observed, i.e., the i.e.p. remained at ~pH 8.8. This result indicates that the silica, both as an impurity with the alumina and from the glass, is inert and essentially insoluble at ~pH 4.5.

These explanations are supported by the fact that the elimination of silica from A-14 alumina by a dissolution process with HF and storing the sample in plastic bottles at ~pH 7 resulted in an i.e.p of ~pH 8.9 and no ageing effect. Similarly, another study<sup>10</sup> has shown that treatment of a feldspar with HF led to electrokinetic values resembling those for alumina indicating that the acid had selectively dissolved the silica. Also, there was no evidence of any effect of  $F^-$  ions on the electrophoretic behavior of alumina or the feldspar. If  $F^-$  ions were adsorbed at the solid/liquid interface, a shift in the isoelectric point would have occurred towards the acid range. Further evidence of the effect of silica is provided by a reverse procedure. When sodium silicate in sufficient amounts to produce, "in situ", equivalent oligomeric species of silica was added to alumina treated with HF, the resultant electrophoretic behavior was similar to the original untreated sample upon ageing both samples in polyethylene bottles at ~pH 7 (Fig. 2f vs. Fig. 2g).

In conclusion it is evident that surface contamination by soluble species from sources such as sample impurities or containers on ageing will lead to erratic values of i.e.p. values. Rheological behavior

of such slurries will vary and will not be reproducible. Undoubtedly, variations in agglomeration, packing and sintering of particles will also occur.

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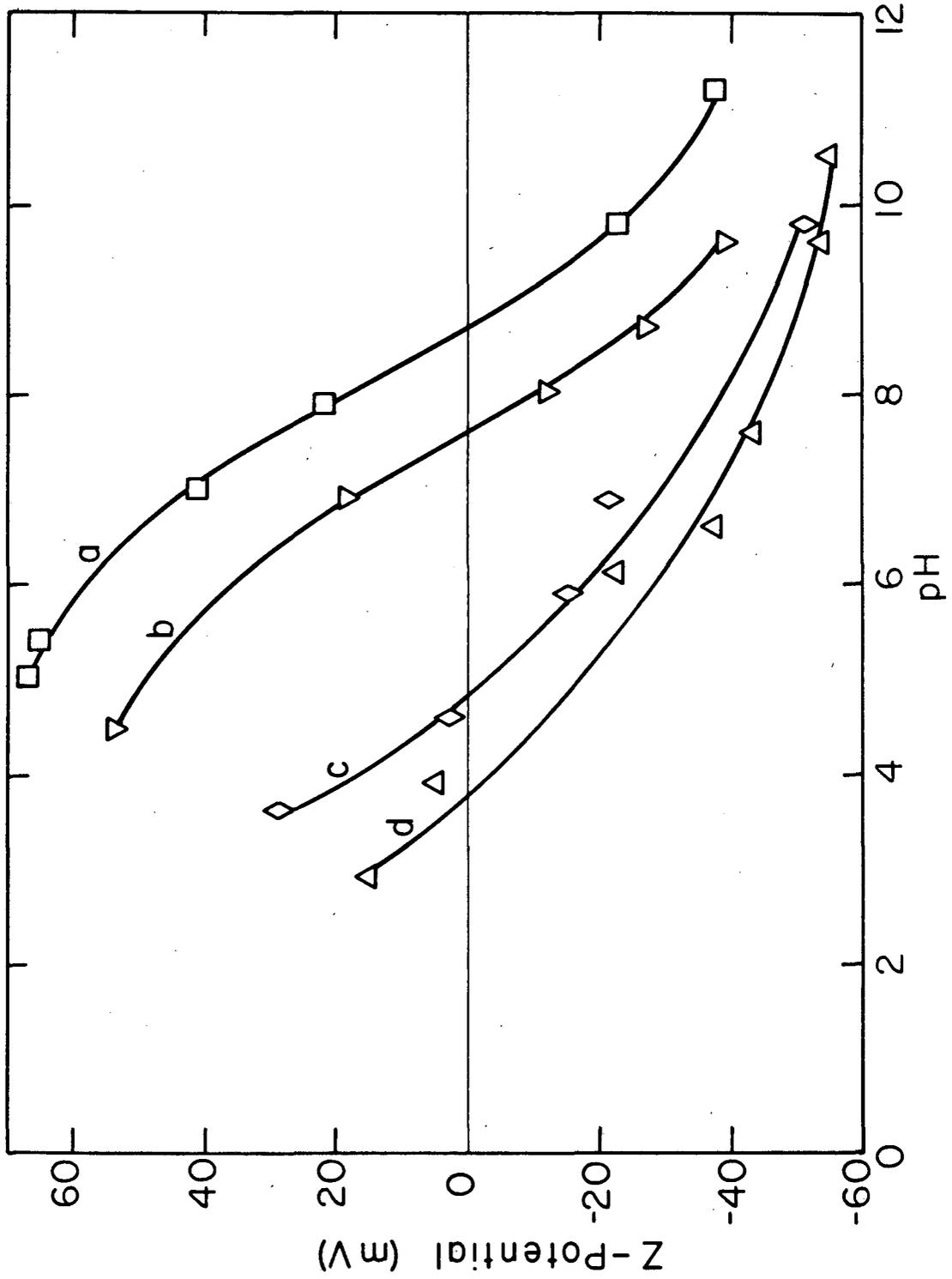
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#### FIGURE CAPTIONS

Fig. 1. Zeta potential vs. pH curves for A-14 samples with different chemical pretreatments and/or equilibration times in pyrex glass containers. (See text for identification of curves).

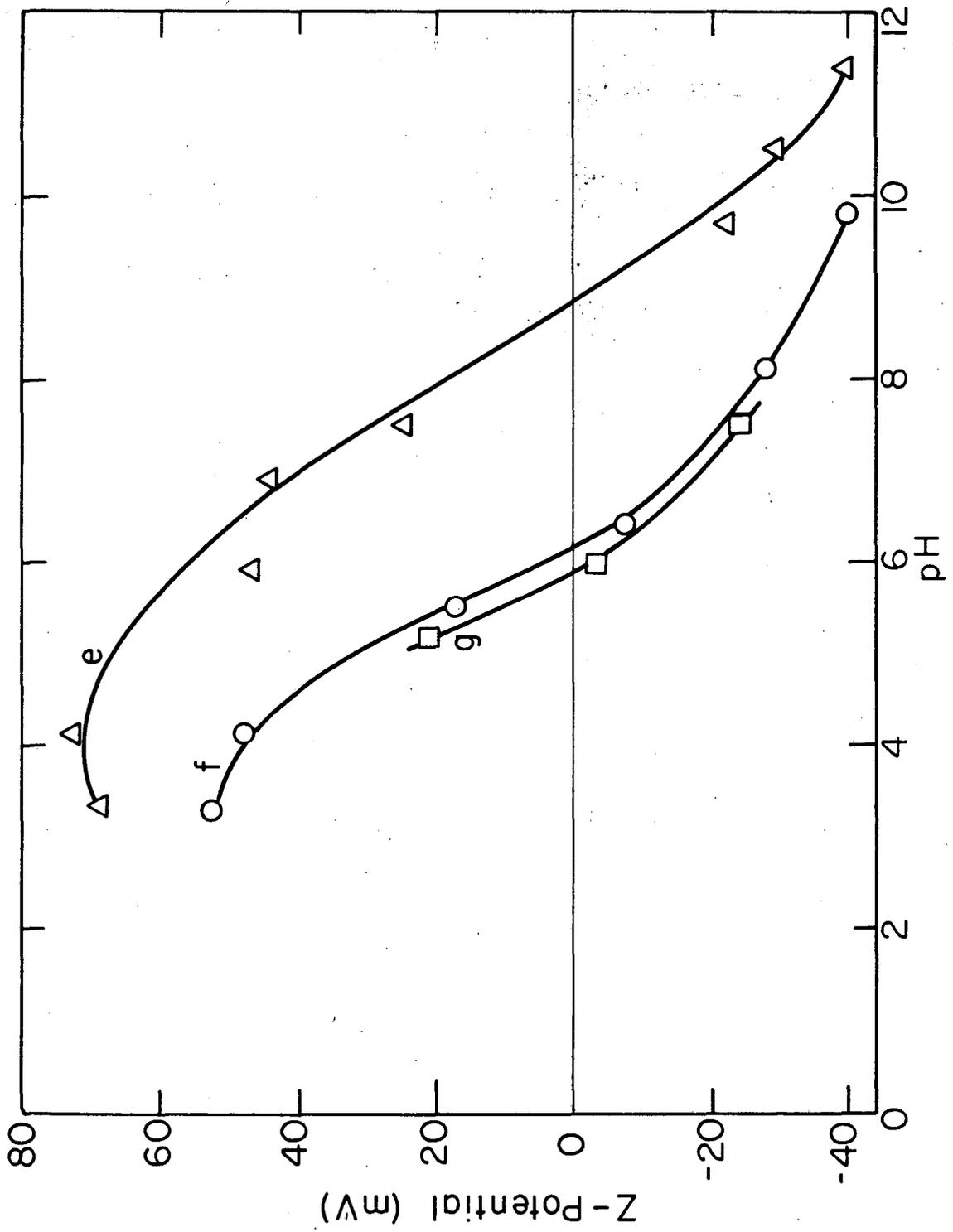
Fig. 2. Zeta potential vs. pH curves for A-14 samples with different chemical pretreatments aged in polyethylene bottles. (See text for identification of curves).

Fig. 3. Isoelectric point vs. square root of times for A-14 and A-12 in different conditions.



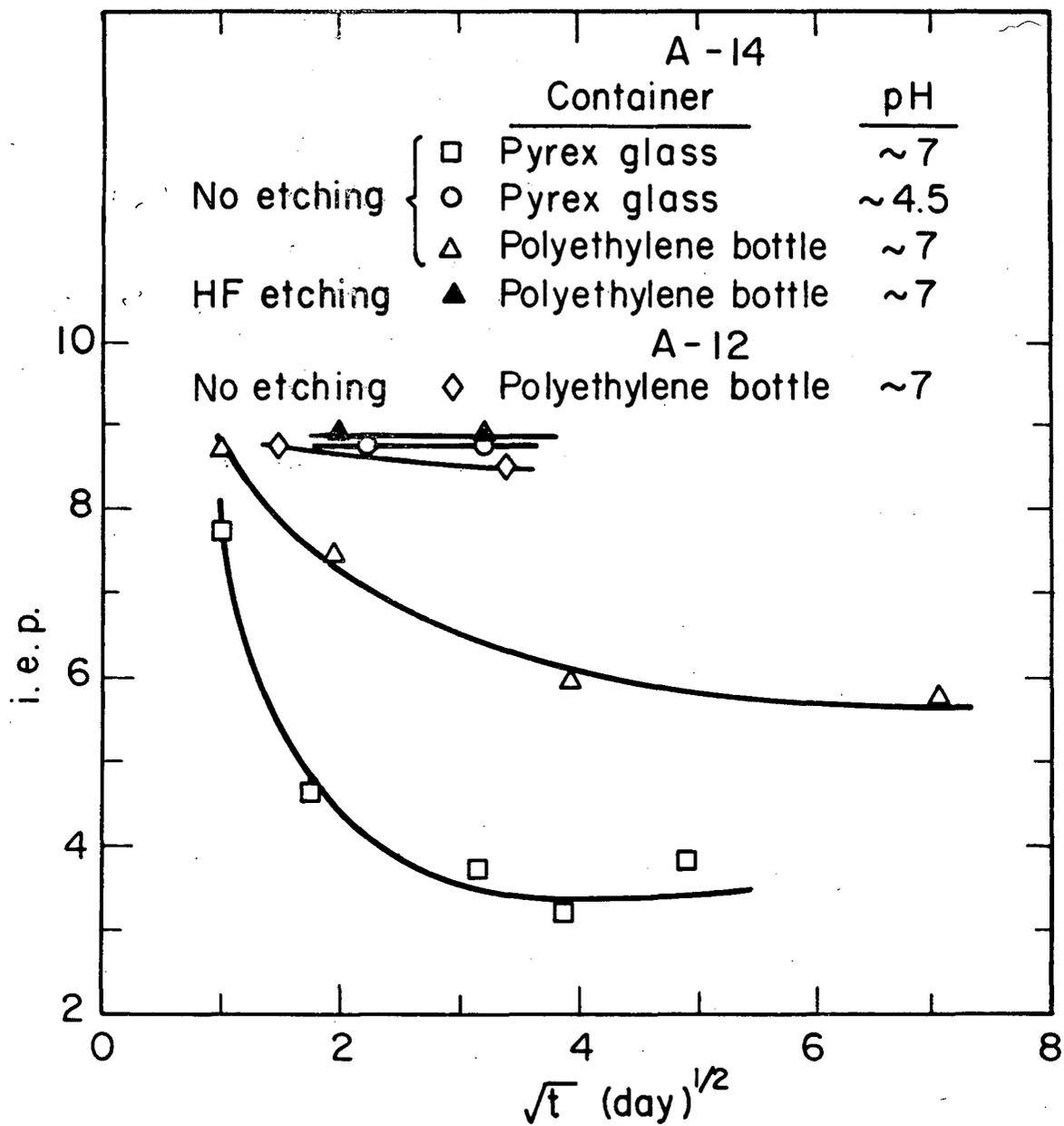
XBL794-6077

Fig. 1



XBL794-6078

Fig. 2



XBL794-6076

Fig. 3

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