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Conference Paper

Electrokinetics of Glass Surfaces. I. Charge Densities at the Solid/Gas and the Solid/Liquid Interfaces of Porous Glasses*

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An attempt is described to determine the charge densities at different layers of the surfaces of glass. Three different techniques were used: the heat-of-immersion technique, the electron spin resonance hyperfine splitting measurements, and the electrokinetic streaming potential or current technique.

Estimates of the charge densities at the various interfaces show the structure can be subdivided into the high and low charge portions. The heat-of-immersion technique, looks into the actual solid surface: there the charge density is estimated at in excess of 10^{14} unit e-charges per cm^2. The hyperfine splitting of the ^{107}Ag ESR spectrum assumed due to the electrostatic field at the site of the localized atom position: a charge density of 0.7 to 1.3×10^{13} is estimated. It is assumed that the Ag atom is localized in the gel-like layer-solution interface. The excess counter-ion charge in the diffuse part of the double layer in the liquid phase is estimated at 3 to 7×10^{12}. Thus, the high charge density plane is the interface solid-gel layer. The estimates are based on independent models of the interface structure, widely accepted in literature, although not entirely free of arbitrary assumptions.

INTRODUCTION

The structure of the interfacial layers between the solid and the liquid or gas phase of various materials (metals, semiconductors, and insulators) has been the concern of electrochemists and of surface chemists for quite a long time. The structure of silica and of glass surfaces has received considerable attention due to the vast importance of these materials in technology. This paper describes an attempt to estimate the charge densities at the surfaces of glass of well defined bulk composition and defined porous structure.

The interfacial layer at the silica or glass surfaces is considered to involve a swollen gel-like layer, situated between the solid surface of glass and the liquid solution[1,2]. It seems that the fixed Helmholtz-type charge layer is located within this layer[3]. Therefore, it is considered, that the diffuse

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double layer model is a good approximation for all the charge interaction and adsorption phenomena involving the particles of glass in contact with the electrolyte solution[4].

EXPERIMENTAL

Materials

Boron-sodium doped high silicate glasses have been used. Produced in the Laboratories of the Inorganic Glass Section of the National Bureau of Standards, they are characterized by controlled pore size and high specific surface areas[5]. Their basic properties are summarized in Table I.

TABLE I

Porous Glass Samples Used in Experiments

Sample Code	Specific surface area, m²/g	Mean pore radius, Å	Pore volume cm³/g	Temperature of heat treatment* °C
BT	96.9	155	0.52	565
BU	47.2	550	1.02	562
BS	10.4	2250	0.74	671
BA	9.0	1630	0.85	650

* Heat treatment used in developing structural domains in the production procedure of controlled pore glasses.

The crushed samples, 50 to 100 Mesh particle size, were treated with hot concentrated nitric acid, washed with redistilled water to constant low value of conductivity on overnight standing and finally treated with triply distilled water free of organic impurities (Water distilled from acid dichromate, alkaline permanganate and followed by distillation from quartz stills).

All the chemicals were of analytical grade (Merck, Darmstadt), and were used without further purification. The same high quality triply distilled water was used in preparation of solutions. Organic liquids: hexane, absolute ethanol, *n*-butylchloride and *n*-butylaldehyde, were high purity chemicals. They were treated with activated Linde 4 A Molecular Sieves and filtered.

Techniques

The heat-of-immersion microcalorimeter was a small Dewar flask immersed in a constant temperature bath of approximately 30 liters, held at 25 ± 0.05° C. The volume of liquid in the immersion part could vary from a minimum of 5 to a maximum of about 25 ml. The basic sensitivity of the microcalorimeter was ± 0.5 mcal* using a thermistor probe od 2 k Ohm resistance and a Wheatstone bridge. The error signal of the bridge was amplified through a microvoltmeter amplifier and recorded on a strip chart recorder.

The glass samples were heated *in vacuo* at 10^{-6} torr** (final) and 300° C for 24 hours in a small glass bulb. Sealed directly off the vacuum line, the sample bulbs were transferred into the microcalorimeter Dewar, temperature equilibrated, and broken. Heat data were corrected for the heat evolved in breaking a blank bulb.

ESR spectra were recorded on a Varian E-3 X-band spectrometer equipped with the automatic field dial control and temperature control accessories.

The samples of glass for the ESR measurements were cleaned as described and then soaked in 10^{-2} *M* $AgNO_3$ solution, or the same solution in which the silver was complexed by adding NH_4OH. Samples were dried in air (or in vacuum when necessary) at room temperature. They were irradiated in ESR vials at liquid nitrogen temperature by X-rays (standard dose 0.1 Mrad) or ^{60}Co γ-rays (standard dose 4 Mrads). ESR spectra were taken at liquid nitrogen temperatures. Differences in the shape of spectra were observed depending on the way of

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* 1 mcal = 4.18×10^{-6} joule

** 1 torr = 1.33×10^{2} Newton/m² preparation of the samples[6]. The hyperfine splitting if recorded, was largely independent of the shape of the central portion of the ESR spectrum.

The electrokinetic streaming potential (at high circuit impedance) or streaming current (at low circuit impendance) experiments were performed as described earlier in detail[7]. Electrolyte solution was allowed to flow through the bed of glass particles in a tube between two unpolarizable Ag/AgCl electrodes. The potential (or IR drop) was measured by an electrometer. The data were treated using the Helmholtz-Smoluchowski equation for calculations of the zeta-potential.

RESULTS

In Figs. 1 and 2 data for the heat-of-immersion measurements are plotted in ergs per cm^2 *vs.* the dipole moment of the liquid for the four types of porous glasses. Calculations of the contribution of polar forces to the interfacial energy[8,9] yield surface charge densities of 0.53 to 1.0 × 10^5 e. s. u. per cm^2,* or 1.1 to 2.1 × 10^{14} unit charge sites per cm^2. Results are tabulated in Table II.

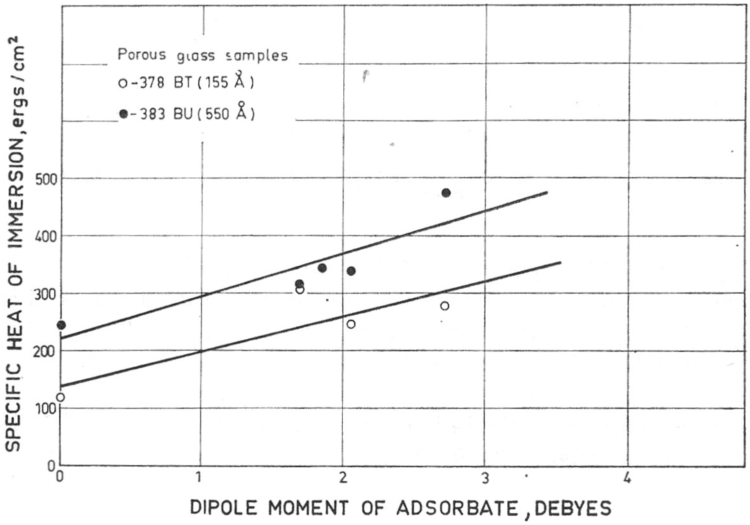

Fig. 1. The specific heat-of-immersion for BT and BU porous glass samples *vs.* the dipole moment of liquid.

TABLE II

Summary of Heat-of-Immersion Data and of Calculated Values

Sample Code	Slope ergs /cm^2/ Debye	Surface field (e. s. u./cm^2) × × 10^{-4}	Density of unit charge sites, cm^{-2} × × 10^{-14}	Relative contribution of polar forces at the water interface
BT	61.4 ± 36.8	8.5	1.8	0.45
BU	73.9 ± 32.6	10.2	2.1	0.38
BS	53.3 ± 25.0	7.4	1.5	0.35
BA	38.5 ± 18.7	5.3	1.1	0.26

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* 1 electrostatic unit = 1 statcoulomb = 3.33 × 10^{-10} coulomb

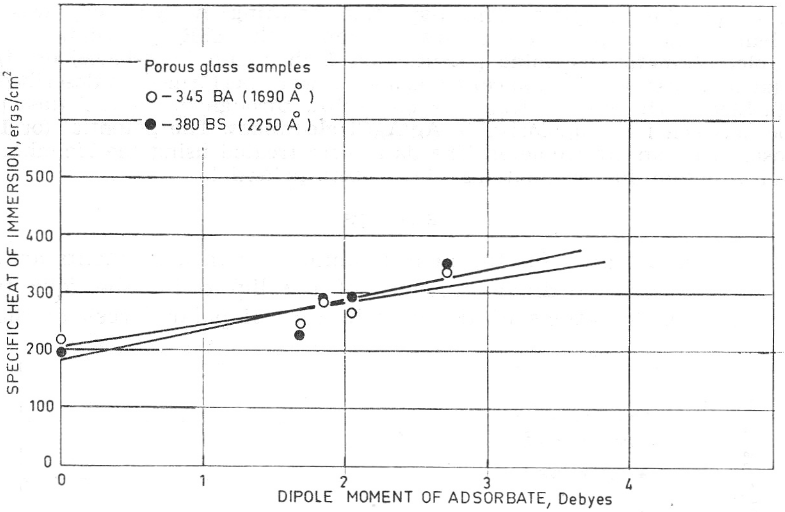

Fig. 2. The specific heat-of-immersion for BA and BS porous glass samples *vs.* the dipole moment of liquid.

In Fig. 3 an ESR spectrum of the BU type glass with adsorbed Ag, obtained at liquid nitrogen temperature is shown. Indication is given of the way of calculating the parameters of hyperfine splitting. In interpreting the spectra the model of Gardner *et al.*[10] was assumed, although the spectra show too narrow lines for surface electrostatic field — spin interactions. The results of the measurements and calculations are summarized in Table III. The values of charge densities range from 0.7 to 1.3 × 10^{13} unit charges per cm².

TABLE III

Summary of ESR Measurements of Hyperfine Splitting for ^{107}Ag Adsorbed on Porous Glass

Sample Code	Hyperfine splitting constant, A (Gauss***)	Hyperfine dimensionless parameter, a (*)	Electrostatic field (V/cm) × 10^{-7}	Density of unit charge sites $cm^{-2} \times 10^{-13}$
BT	610.2	0.9976	2.2	1.3
BU	612.0	0.9991	1.2	0.66
BS	611.8	0.9990	1.2	0.66
BA**	612.6	0.9997	0.9	(0.50)

* Values for A_0 for ^{107}Ag in equation $a = (A/A_0)^{1/2}$, were taken as 613.0 Gauss. See Ref. 10 for details.

** Sample dried *in vacuo* after adsorption of Ag^+. No hyperfine splitting was observed under standard treatment (air and room temp.)

*** 1 Gauss = 10^{-4} Weber/m²

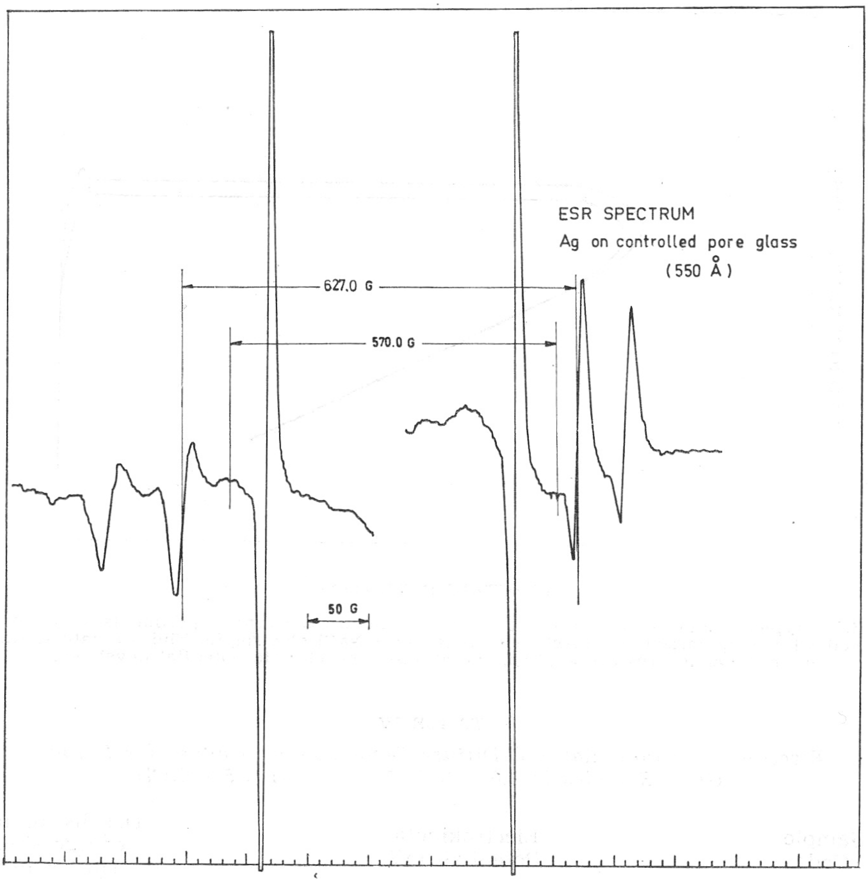

Fig. 3. The ESR spectrum for Ag adsorbed on porous glass type BU. The central portion of the spectrum is omitted. Graphical estimation of hyperfine splitting is indicated.

Fig. 4 shows a typical response of the measurement device for the streaming current experiment: conditions were found where the response of the system is reproducible, and the dependence of the potential on hydrodynamic pressure linear. Data of such quality were used in compiling the results shown in Table IV. The 10^{-4} *M* NaCl solution was chosen to minimize the influence of surface conductance[11] and still have low concentration conditions allowing the approximation $\zeta = \psi$ potential[12]. From the values shown in Table IV for the ζ-potential the surface charge density was calculated using the Gouy-Chapman model of the diffuse double layer. The values between 3 and 7×10^{12} unit charges per cm^2 indicate the lowest values in the three different interfaces studied.

DISCUSSION

In contrast to the model of the double layer used in interpreting interface properties of metals and simple metal oxides (nonswelling), the interface glass/solution is assumed to consist of two boundaries. At the solid surface

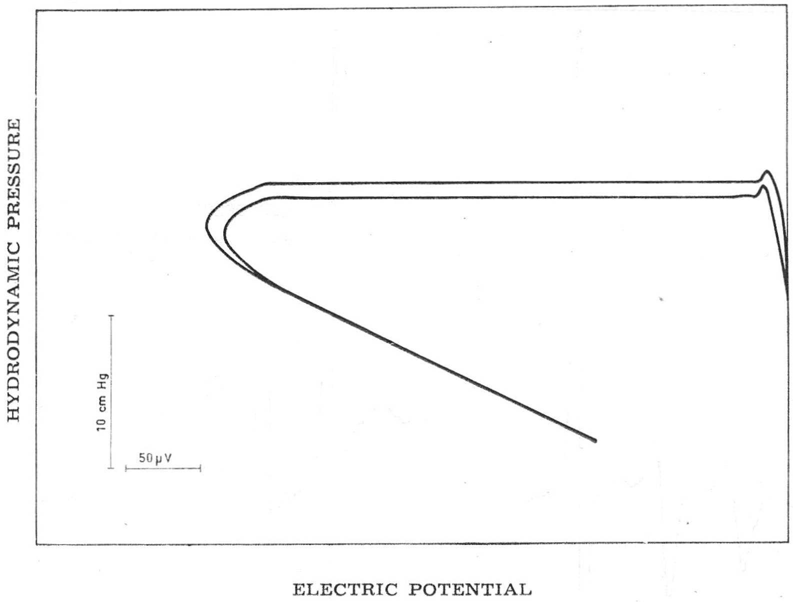

Fig. 4. A typical response curve for duplicate streaming current experiments with powders in a cell with nonpolarizable Ag/AgCl electrodes in a NaCl electrolyte. The ordinate shows the hydrodynamic pressure applied, the abscissa the electric potential developed.

TABLE IV

Electrokinetic Potential and Diffuse Double Layer Charge for Porous Glass Samples in 1.0 × 10^{-4} M NaCl, pH = 5.0 (HCl)

Sample Code	Electrokinetic Potential, mV	Density of unit charge sites* $cm^{-2} \times 10^{-12}$
BT	108	3.3
BU	120	4.2
BS	136	5.8
BA	142	6.6

* The Gouy-Chapman model of the diffuse double layer is assumed and the charge density calculated from[12]: $\eta = (RTc/2\pi)^{1/2} \times 2 \sinh (zF\zeta/RT)$

proper adsorption of water causes swelling and formation of a gel-like layer. Indirect measurements of Watillon[2] indicate a maximum thickness of up to 80 Å. Most of the potential drop of the interface is located in this layer. The double layer in the solution side of the interface is then quite properly represented by the diffuse double layer model[13]. Indeed, it is difficult to assume a distance of closest approach of cations and the existence of a Helmholtz type layer. A cation would penetrate the gel layer by diffusion. This assumption has been used by Lyklema[14] in developing the concept of the porous double layer. In this model of the double layer part of the charge is accomodated behind the surface. It seems that the present measurements of ESR hyperfine splitting and the resulting charge densities would speak in favor of this model. An alternative approach to the problem of highly charged oxide/solution interface has been advanced by Bérubé and De Bruyn[15] who have postulated a model in which the hydroxyl ions (potential determining ions for oxide interfaces) are not situated in a plane adjacent to the solid surface but separated from it by one or more than one layer of water molecules. It is difficult to reconcile the present results with this model.

In the immersion experiments an original solid surface is assumed to come into contact with the polar liquid. Hockey has shown by IR measurements[16] that the last hydroxyl groups are still not removed from the surface even at prolonged heating to 500° C. But, there was no evidence of the existence of a gel layer. Therefore the treatment of glass used here insured the production of a hydroxylated solid surface. From data on heats-of-immersion, one can following Zettlemoyer[8,9] calculate the contribution of polar forces to the total interface energy. On inspecting data in Table II and recollecting that the total number of surface sites at such a glass surface is about 7×10^{14} cm^{-2}, it follows that one out of three to five sites carries a charge. No assumption is made as to the origin of surface charge. The next step in following these lines of thought was to measure the charge in the gel layer. Experiments of Zhitnikov and Paugurt[17], and those along with the theories of Gardner, Casey, and Grant[10] were based on the assumption that the released free Ag atom would migrate to the site of highest energy and remain there. The hyperfine splitting would then reflect the contribution of surface electrostatic forces. The question is: where in the interface is the Ag atom actually located and what field does it »see«? The assumption made here is that the location of the Ag atoms is in the gel like layer, but due to the low temperature its diffusion is highly retarded. Consequently, one would expect the Ag atoms located near the gel-solution interface. The calculated charge densities fit nicely into this picture. They are considerably higher than those in the solution side, but still an order of magnitude less than at the solid surface.

The electrokinetic experiments were believed to reflect the situation at the gel-solution interface. As mentioned before the concentration of electrolyte and the *p*H were chosen to provide for an electrokinetically stabilized, reproducible interface[18]. The surface conductance correction in negligible[11], the double layer not compressed and the plane of shear should coincide with the gel-solution interface. If these assumptions are accepted as correct then the calculated charge densities indicate that only a small fraction of the total interface charge is located in the solution proper.

Porous glass has proved a convenient experimental model material due to its large specific surface area. The pore sites are also large with respect to ionic or molecular dimensions of the components of the system investigated, and therefore no charge accumulation in the sense of the Lyklema model is due to such a structure. And finally, although the techniques and methodology of experiments described involve models which are not entirely free of arbitrary assumptions, the conclusions may be considered as representative for surfaces of borosilicate glasses of any particle shape.

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IZVOD

Elektrokinetika staklenih površina. I. Gustoća naboja na granici faza čvrsto/plinovito i čvrsto/tekuće uzoraka poroznih stakala

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Raspodjela polja, odnosno gustoće naboja na granici faza staklo—elektrolitna otopina, proučavana je različitim metodama. Mjerenjem toplina kvašenja na visokoj temperaturi osušenih uzoraka u nizu tekućina raznog dipolnog momenta dobiven je doprinos polarnih sila ukupnoj energiji čvrste površine. Ustanovljeno je da gustoća nabijenih mjesta iznosi između 1,1 i $2{,}1 \times 10^{14}$ po cm^2, tj. da je svako treće do peto mjesto na površini nabijeno jediničnim nabojem. Mjerenjem hiperfinog cijepanja u spektru elektronske spinske rezonancije za Ag atom, adsorbiran u gel-sloju na površini stakla, ustanovljeno je da je u tom sloju gustoća naboja za red veličine manja od one na čvrstoj površini, i da iznosi od 0,7 do $1{,}3 \times 10^{13}$ po cm^2. To dozvoljava pretpostavku da je na granici faza staklo—otopina najveći dio pada potencijala graničnog sloja lokaliziran u gel-sloju. Konačno je elektrokinetičkim mjerenjima potencijala, ili struje strujanja, utvrđeno da je gustoća naboja u difuznom dijelu dvosloja u fazi otopine sumjerljiva gustoći naboja u gel-sloju. Time je pokazano da je naboj, lociran u fazi otopine, samo neznatan dio ukupnog naboja granice faza staklo/elektrolit.

Iako ova razmatranja nisu neovisna o nekim arbitrarnim pretpostavkama vezanima uz metodologiju eksperimenata, ipak se smatra da je odgovor o raspodjeli naboja od općeg značenja za sve granice faza borosilikatnih stakala u kontaktu s elektrolitnim otopinama.

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