

Multiinstrument Study of the Electrophoretic Mobility of Fumed Silica

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Although silica is one of the most common adsorbents, the position of its isoelectric point (IEP) on the pH scale remains an open question. Different values from 1 to 4 have been published, and there is even a controversy about the very existence of the IEP. The discrepancies in the literature are at least partially due to application of different instruments. Different zetameters produce different ζ potentials of silica in the acidic range and different IEP.

The surfaces of sparingly soluble metal oxides are amphoteric; i.e., they carry positive charge below and negative charge above their points of zero charge (PZC) (the pH at which the net surface charge equals zero). The PZC of common metal oxides in the absence of strongly adsorbing species are well established in the literature,¹ and they can be determined using different independent methods. Numerous theories have been proposed to derive the position of the pristine PZC (PZC in the absence of specific adsorption, e.g., in dilute solutions of alkali nitrates, chlorates VII, and halides) of metal oxides from their physical properties.¹ The PZC should be clearly distinguished from the isoelectric point (IEP), defined as the pH at which the electrokinetic potential equals zero. At pristine conditions, the PZC and IEP of pure metal oxides match, but they are obtained using different experimental methods.

Silica carries negative surface charge over the usually studied pH range 3–10. By analogy with metal oxides, the silica surface is often deemed amphoteric too, although there is a controversy about the very existence of PZC,² and if the PZC does exist, its position is very unsure. First, the number of methods applicable to find the PZC at low pH (<3) is limited. For example, potentiometric titration of metal oxides at different ionic strengths produces a distinct common intersection point which is identified with the PZC. With silica, the titration curves do not intersect but they rather merge at low pH. Moreover, the apparent surface charge density at low pH is obtained as a difference of two large and almost equal numbers; thus, the calculated sign of the surface charge is of limited significance. Therefore, electrokinetic mea-

surements are usually employed to locate the PZC of silica. A few other methods described in detail elsewhere¹ have been also proposed, but their significance is limited.

The results published in the literature are controversial. Most electrokinetic studies report only negative values of the ζ potential of silica, and some authors obtained "IEP" beyond the experimental range using extrapolation. Extrapolated IEP are rather commonplace, also in citations and compilations, but they have limited significance. Actual IEP (positive ζ potentials at sufficiently low pH) was also found for some samples of silica, and it should be clearly distinguished from the extrapolated IEP.

The actually measured (not extrapolated) IEP for silica are diverse and they range from pH 1 to 4; many studies suggest the absence of any IEP at all even at a pH as low as 1. This discrepancy is more significant than the scatter in the PZC for common metal oxides (a few outstanding values reported in the literature for metal oxides are due to experimental errors or insufficient purity). Some outstanding results for silica may be also due to experimental errors, but the diversity of the IEP of silica suggests rather the existence of some important factor that remains beyond control. Numerous attempts to find some rationale for such diversity have been made.

The most obvious hypothesis is that the IEP varies from one sample to another reflecting the difference in the structure; namely, the surface acidity is related to the bond length, which in turn is structure dependent. The average IEP of quartz samples published in the literature is indeed somewhat lower than the average IEP of amorphous silica samples, and quartz was considered more often than amorphous samples to have no IEP, but relatively high IEP (~3) as well as results suggesting the absence of any IEP have been found for either type of material.¹

Publications reporting on systematic research of the effects of impurities on the IEP of silica are scarce, and they do not lead to unequivocal results. For instance, no clear correlation was found in a series of reagent grade silicas (used as obtained and purified) between the level of metallic impurities (Al, Fe) and the IEP.³

The other rational explanation would be that some electrolytes, which behave indifferently against metal oxides, are capable of shifting the IEP of silica at relatively low concentrations. In other words, not necessarily are all 1–1 electrolytes inert with respect to silica. Existence of the IEP at pH 2 in the presence of chlorides

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Table 1. Instruments Used To Measure the ζ Potential, and Experimental Conditions

brand name	Pen Kem	Malvern	Coulter	Colloidal Dynamics	Dispersion Technology
type	Laser Zeometer 501	Zetasizer 3000	Delsa 440	Acustosizer	DT 1200
principle of operation	electrophoresis, measurement at the stationary level	electrophoresis, stationary-level problem-free cell	electrophoresis, parabola method	electroacoustic effect, no background correction	colloid vibration current (preassumed particle size of 0.2 μm)
mass fraction of silica (%)	0.01	0.01	0.02–1	5	3
equilibration time at initial pH	overnight	overnight	overnight	overnight	overnight
equilibration time, other data points	overnight	overnight	20 min–1 h (titration starting at pH 2 or 8)	20 min–1 h (titration starting at pH 2 or 8)	20 min–1 h (titration starting at pH 2 or 8)

and nonexistence in the presence of nitrates and chlorates VII was suggested,⁴ but publications reporting the ζ potential of one silica sample in the presence of different anions are scarce. On the other hand, there is a strong evidence in the literature¹ that potassium salts at concentrations above 0.01 mol dm⁻³ induce a shift in the IEP of silica to high pH.

It seems obvious that all zetameters should produce the same value of the ζ potential for given sample, but this is not necessarily true. The ζ potential just above or just below the IEP is usually low, especially at high ionic strength. Thus, a few millivolt error in the value of ζ potential may produce a substantial shift in the IEP. In the present paper, we compare ζ potentials obtained for silica using different instruments and discuss probable reasons for some discrepancies.

EXPERIMENTAL SECTION

Fumed silica was Aerosil 380 from Aldrich, and according to the manufacturer, it is practically free of metal ions. Material from the same lot and in most cases from the same jar was used in all experiments as received, without purification.

The sample was characterized by potentiometric titration at NaCl concentrations of 0.01, 0.1, and 1 mol dm⁻³. The surface charge density was calculated as $\sigma_0 = -\Delta VcF/(mA)$, where ΔV is the difference in the volume of c molar NaOH solution that is necessary to bring a dispersion containing mass m of silica of specific surface area A on one hand and blank solution (without silica) on the other to the same pH, and F is the Faraday constant. The equilibration times were at least 1 h before the titration and 20 min for each data point, and the titration was carried out in a nitrogen atmosphere. More details regarding this technique and its limitations can be found elsewhere.¹

The ζ potential of amorphous silica was determined at the ionic strength of (roughly) 10⁻² mol dm⁻³ at pH 2–8. Reagent grade NaOH, HCl, HNO₃, NaCl, and NaNO₃ were used in different combinations to establish the pH and ionic strength. MilliQ water was used in most experiments, but a few measurements with quartz distilled water were performed for comparison. The instruments used in this study and the experimental conditions are briefly characterized in Table 1. The ζ potentials were calculated from the measured mobility by means of the Smoluchowski equation. All measurements were carried out at 25 °C.

The pH measurements were performed using standard procedures recommended in the user manual. The readings were taken once they became stable, which took from ~1 min to a few

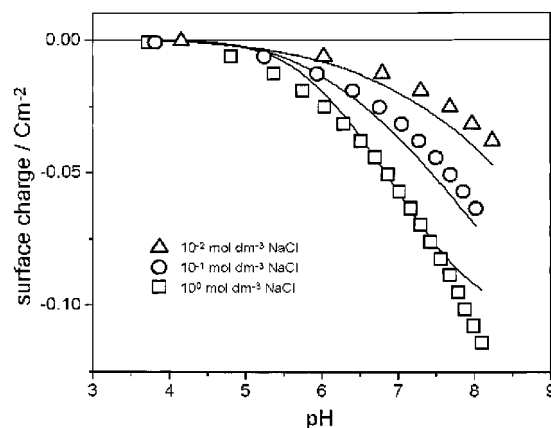


Figure 1. Experimental and calculated surface charge density of silica as a function of pH and ionic strength.

minutes. Four different pH meters and different pH electrodes were used. This was to some degree unavoidable; e.g., Acustosizer and DT-1200 have their built-in pH meters.

RESULTS AND DISCUSSION

The surface charge density σ_0 of Aerosil as a function of the pH is presented in Figure 1. The σ_0 was independent of the solid-to-liquid ratio (0.5–2 g/50 cm³). The model curves represent the diffuse layer model with pK_a 6.51 and 0.65 sites nm⁻². In the model calculation, the display of the pH meter was identified with the activity of protons and the activity coefficients of other ionic species were calculated from Davies' formula. The above model is not unique, and other models or other sets of parameters within the same model produce similar model curves. For example, for 4.5 sites nm⁻², the best-fit pK_a is 7.54. Both pK_a fall in the range typical for amorphous silicas, but they are substantially lower than the pK_a of monosilicic acid and substantially higher than the pK_a of quartz.^{5,6}

The nature of the anion (chloride vs nitrate) and the quality of water (MilliQ vs quartz distilled) do not significantly affect the ζ potential of Aerosil over the studied pH range. The relative insignificance of the nature of the anion is illustrated in Figure 2 using the results obtained by means of Malvern Zeta Sizer. In subsequent figures, we only present representative results without specifying the nature of the anion.

The ζ potential was also rather insensitive to aging of the dispersion at acidic or basic pH for 1–20 h; i.e., acid titration of

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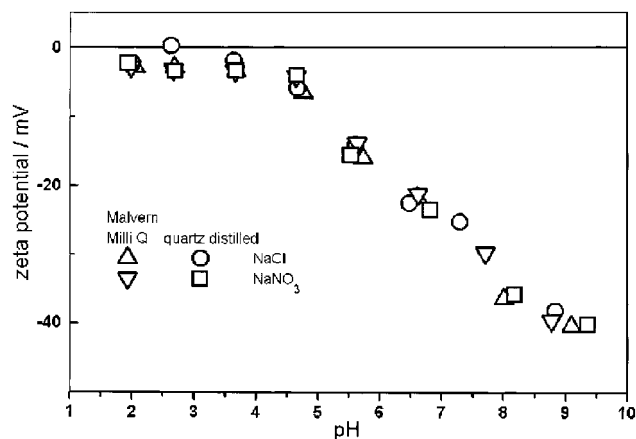


Figure 2. ζ potential of silica in 0.01 mol dm^{-3} NaCl and NaNO_3 in MilliQ water and quartz distilled water measured by the Malvern Zeta Sizer 3000.

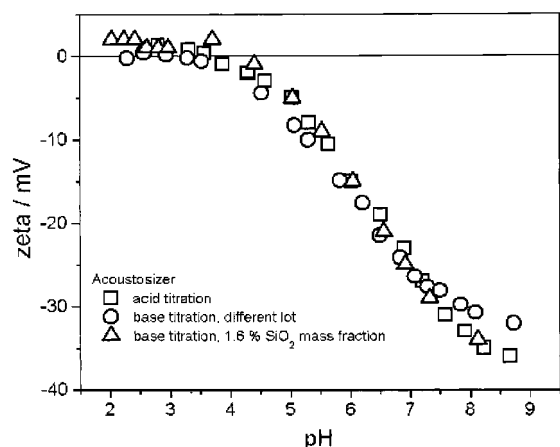


Figure 3. ζ potential of silica measured by the Acoustosizer (acid and base titration, different solid-to-liquid ratios, two different lots of silica) at an ionic strength of 0.01 mol dm^{-3} .

the dispersion pre-aged at basic pH and base titration of the dispersion pre-aged at acidic pH produced very similar results (within 2 mV). The ζ potentials previously obtained with a different lot of the same type of material coincide with the present results (Figure 3). The rate of titration (20-min vs 1-h equilibration at given pH) does not affect the results.

The ζ potentials measured by means of different instruments are presented in Figure 4. These results show that the apparent IEP from <2 (if any, Malvern), ~ 2 (Pen Kem), to ~ 4 (three other instruments) can be obtained for the same silica sample. This range roughly corresponds to the ranges in which the IEP of different silica samples are reported in the literature.^{7–22} On the

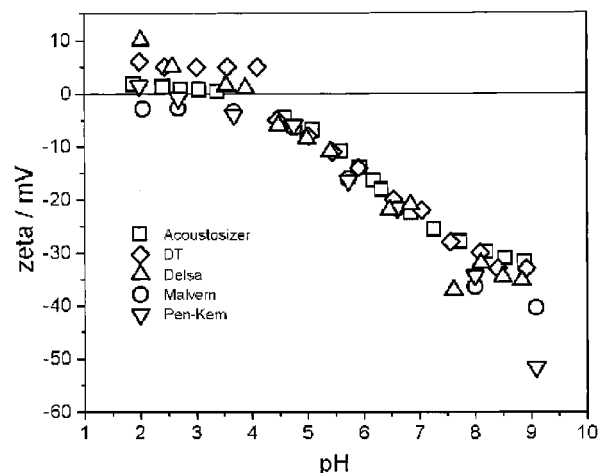


Figure 4. ζ potential of silica measured by five different instruments at an ionic strength of 0.01 mol dm^{-3} .

other hand, the electrokinetic curves over the pH range 4–8 are very consistent.

Different solid-to-liquid ratios can be responsible for the discrepancies. The lowest IEP was obtained with Malvern and Pen-Kem instruments, and the solid-to-liquid ratio was lower than with the other instruments. With the DT and Acoustosizer, some background correction (which is immaterial for high negative ζ potentials) may change the position of the IEP. The difference between DT and Acoustosizer is probably caused by a different method of calculation (preassumed particle size in DT).

Figure 5 shows the same experimental data from Pen Kem as Figure 4, a set of experimental points taken from ref 17 (Aerosil 380, 0.01 mol dm^{-3} NaCl, temperature not reported, IEP at pH 3.8), obtained using the Zetaphoremeter II Sephy 2100 (France), and the line representing the surface potential calculated with the same model parameters as the model curves in Figure 1. The measured ζ potential is approximately equal to the calculated surface potential at low pH, and substantially lower at high pH. This result is in line with low counterion adsorption on silica at low pH and substantial counterion adsorption at high pH.¹ More sophisticated models are necessary to quantitatively account for this effect. This figure also shows the consistency of our results and those reported in the literature (except for the position of the IEP).

The present results suggest that the discrepancies in the literature data are caused by using different instruments. To examine this hypothesis, a few IEP reported in the recent literature^{4–22} for commercially available reagent grade amorphous silicas were sorted by the instrument (trade name, which usually represents different versions of the instrument). Different samples

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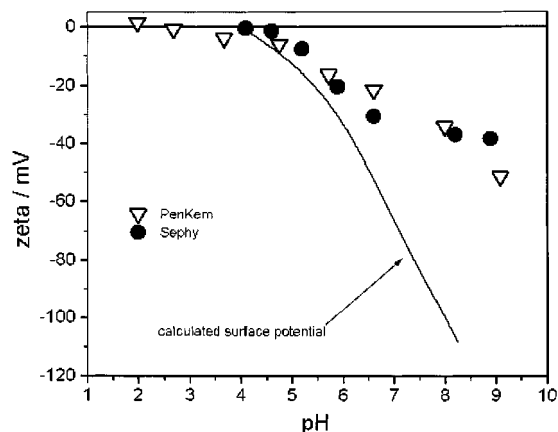


Figure 5. ζ potential of silica measured by the Pen Kem at an ionic strength of 0.01 mol dm^{-3} , the results from ref 17 (the same material and conditions except the temperature is not reported), and surface potential calculated using a diffuse layer model.

Table 2. ζ Potentials of Commercially Available Reagent Grade Amorphous Silicas Reported in the Literature

instrument	Malvern	Pen Kem	Brookhaven	other
no. of entries with only negative ζ (no IEP)	2	1	3	1
no. of entries with IEP	3	1	5	3
IEP range	2.9–3.2	3.8	1.6–3.8	1.9–3.7
average IEP	3.03	3.8	2.47	2.76

of silica were studied in different 1–1 electrolytes and at different electrolyte concentrations. The temperatures were also different and not always reported. The results are summarized in Table 2. We did not find publications reporting the ζ potentials of commercially available reagent grade amorphous silicas obtained by Delsa, but the results reported for Stöber silica^{23,24} suggest that this instrument tends to produce relatively high IEP in

accordance with Figure 4. We did not find publications reporting the ζ potentials of commercially available reagent grade amorphous silicas obtained by Acoustosizer except for previously published results from the same laboratory. Table 2 does not reveal any dramatic difference between Malvern (the only instrument that did not produce an IEP in our study, Figure 4) and other instruments. Thus, the conclusion that certain instruments produce systematically higher IEP of silica than others obtained in direct experimental study was not confirmed by the literature survey. However, the present results clearly show that allegations as to the existence or nonexistence of IEP of certain samples of silica based on a single instrument study are of limited significance.

The discrepancies in the IEP of silica the present paper and in the literature may be to some degree due to different electrodes and procedures used to measure the pH. Most publications on electrokinetic potentials of silica do not report on details of pH measurements. The discrepancies in the IEP exceeding one pH unit are rather unlikely to be solely due to errors in pH measurements, and consistency in the ζ potentials obtained at high pH confirm that different pH meters produce consistent results. A systematic study of possible effects of different electrodes and procedures used to measure the pH on the position of the IEP of silica (and other materials) is necessary to ultimately solve this problem.

A freshly prepared dispersion of Aerosil 380 in 0.01 mol dm^{-3} NaCl or NaNO₃ (aged for a few hours to a few days) adjusted to pH ~ 7 with NaOH can be suitable as a ζ potential standard. The necessity to prepare the dispersion from dry powder and pH adjustment does not necessarily have to be considered as a disadvantage. Preparation of such dispersions is easy (apparently the solid-to-liquid ratio does not affect the ζ potential so it can be adjusted for the optimum performance of the zetameter of interest), and in contrast with premixed dispersions, such a standard has practically unlimited shelf time in the dry state.

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