

Multiinstrument Study of the Electrophoretic Mobility of Quartz

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The electrophoretic mobility of quartz in 0.01 mol dm⁻³ NaCl and NaNO₃ over the pH range 2–8 was studied using five different commercial instruments. The mobilities over the pH range 4–8 were relatively consistent, but the mobilities over the pH range 2–4 and the position of the isoelectric point IEP varied from one instrument to another. This result suggests that the discrepancies in the apparent IEP of quartz (and other silicas) reported in the literature are due to the instrument artifacts. © 2002 Elsevier Science (USA)

Key Words: quartz; isoelectric point; zeta potential; silicon IV oxide; electric double layer.

INTRODUCTION

It seems obvious that all commercially available zetameters should produce identical results for a given colloid. So obvious, that this statement is not explicitly pronounced, and consequently it has not been verified or challenged.

The discrepancies in the position of the IEP of amorphous silica reported in the literature and the controversy about the very existence of the IEP (1) have been recently attributed to instrument artifacts (2). Namely, the position (or even existence/nonexistence) of the IEP of fumed silica (reagent grade, powder from one jar was used in all experiments) depends on the choice of the zetameter. Reference (2) points out that the (hypothetical) consistency of results produced by different zetameters needs verification. In the present study five different zetameters were used to measure the electrokinetic mobility of quartz at otherwise identical conditions.

The goal of this multiinstrument study is to examine:

- consistence in the IEP obtained by means of different zetameters for the same sample of quartz
- correlation between the instrument artifacts observed for two types of silica (quartz and fumed silica)
- relationship between the IEP of quartz and fumed silica.

LITERATURE SURVEY

Many electrokinetic studies of quartz have been reported in the literature. For the present analysis a few recent studies (3–22)

were selected, in which:

- the ζ -potential or electrophoretic mobility as the function of pH is explicitly reported (the publications reporting only the numerical values of IEP, without the primary data, were ignored)
- aqueous solution of alkali nitrate, chlorate VII or halide or of one of the corresponding acids at a concentration below 0.1 mol dm⁻³ is the supporting electrolyte
- the trade name of the zetameter or at least the principle of the measurement (electrophoresis vs streaming potential) is reported.

The details on experimental conditions (temperature, nature, and concentration of supporting electrolyte), also for the electrokinetic studies of quartz not used in the present analysis, are summarized elsewhere (23). The results are interpreted as follows:

- the IEP was obtained by graphical interpolation when at least one positive value of the ζ -potential or electrophoretic mobility was reported
- the studies in which no positive ζ -potentials (electrophoretic mobilities) are reported are interpreted as “no IEP” (“IEP” obtained by extrapolation are not taken into account)
- when zero is the highest ζ potential reported, the results are also interpreted as “no IEP.” Namely, such a data set does not positively prove that the sign of ζ potential is reversed to positive at sufficiently low pH. Equally well the ζ potential can asymptotically tend to zero (with some scatter). In other words “no IEP” means “no positive proof of existence of the IEP” rather than “positive proof of nonexistence of the IEP.”

The numerical values of the IEP evaluated from the literature data using the above criteria are sorted in Table 1 by trade names of the zetameters. It should be emphasized that one trade name usually represents different versions of the instrument. Most electrokinetic studies of quartz resulted in negative ζ potentials over the entire studied pH range. The other studies which resulted in a few positive values of ζ potential (at sufficiently low pH) are rather randomly distributed between different instruments. The measurements of streaming potential produce positive ζ potentials (thus suggest existence of an IEP) more often (60% of the entries in Table 1) than the measurements of electrophoretic mobility (24% of the entries), but the literature

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TABLE 1
IEP of Quartz Reported in the Literature

Instrument, brand name	Number of entries without IEP	Reported values of the IEP
Pen Kem	2	1.8
Brookhaven	1	
Zeta Meter	4	2.3
Rank	1	2.5
Malvern	2	4.2
Other (electrophoresis)	3	
Other (streaming potential)	2	1.5, 2, 3

survey does not indicate any correlation between the types of commercial zetameters and apparent existence/nonexistence of IEP. A vast majority of the results shown in Table 1 (electrophoresis and streaming potential summed up) does not support the hypothesis of existence of the IEP for quartz. Analogous analysis for amorphous silica (2) suggest the contrary: 63% of cited papers report positive ζ potentials for amorphous silica, i.e., positively proof the existence of an IEP.

EXPERIMENTAL

The original quartz powder, Sikron SF 800, was a gift from Quarzwerke GmbH, Frechen, Germany. According to the manufacturer the average corn diameter is 2 μm , the BET surface area is 6 m^2/g , and it contains 0.3% Al_2O_3 , 0.05% Fe_2O_3 , 0.1% $\text{CaO} + \text{MgO}$, and 0.2% $\text{Na}_2\text{O} + \text{K}_2\text{O}$ (by weight). The original material was washed with hydrochloric and/or nitric acid to remove metals.

The pH (2–8) and ionic strength of (about) $10^{-2} \text{ mol dm}^{-3}$ of the quartz dispersions were adjusted using reagent grade HCl, NaOH, HNO_3 , NaCl, and/or NaNO_3 . MilliQ water was used in most experiments but a few measurements with quartz distilled water were performed for comparison. All measurements were carried out at 25°C.

The trade names of the zetameters and the experimental conditions is summarized in Table 2. With Pen Kem and Malvern,

each dispersion was separately prepared from dry powder. With other instruments, one dispersion was prepared, the pH values were adjusted step by step by addition of NaOH (base titration) or HCl or HNO_3 (acid titration). Each titration curve presented in the figures represents a freshly prepared dispersion which was only titrated in one direction (acid or base titration).

The electrophoretic mobility was converted into ζ potential by means of the Smoluchowski equation.

RESULTS AND DISCUSSION

Figure 1 shows the results of zetametric titration (carried out by means of Acustosizer) of the original powder and of two lots of washed quartz:

- lot 1—washed using 1 molar HNO_3 (3 days, fresh acid every day) and water (10 cycles of rinsing/centrifugation that took together 1 day).
- lot 2—washed using 1 molar HCl (3 days, fresh acid every day), then 1 molar HNO_3 (1 day), and then water (10 cycles of rinsing/centrifugation that took together 1 day).

All three materials, especially the unwashed, original quartz show substantial hysteresis. The hysteresis could not be avoided even by very slow titration (equilibration for many hours without addition of acid or base). The general trend is always the same, i.e., base titration produces less negative ζ potentials than acid titration. The discrepancies are most pronounced at pH about 5, and the acid and base titration curves merge at very low or very high pH. Such a “memory effect” (the ζ potential corresponds to some past pH rather than to the present pH of the dispersion) is commonplace in zetametric titrations, and it has been reported for many other materials.

Surprisingly, base titration of the raw material results in the increase in the ζ potential until pH 4.5. Above pH 4.5 quartz behaves as expected, i.e., further addition of base gives more negative ζ potentials. Electrokinetic curves of silica with such a maximum indicate the presence of specifically adsorbed metal

TABLE 2
Instruments Used to Measure the ζ Potential, and Experimental Conditions

Brand name	Pen Kem	Malvern	Coulter	Colloidal Dynamics	Dispersion Technology
Type	Laser Zeemeter 501	Zetasizer 3000	Delsa 440	Acustosizer	DT 1200
Principle of operation	electrophoresis, parabola method	electrophoresis, stationary-level-problem-free cell	electrophoresis, parabola method	electroacoustic effect, no background correction	colloid vibration current, no background correction
Mass fraction of silica	0.01%	0.01%	0.02–1%	5%	7%
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)
Number of data points averaged	≥ 5	≥ 5	≥ 2	≥ 2	≥ 2

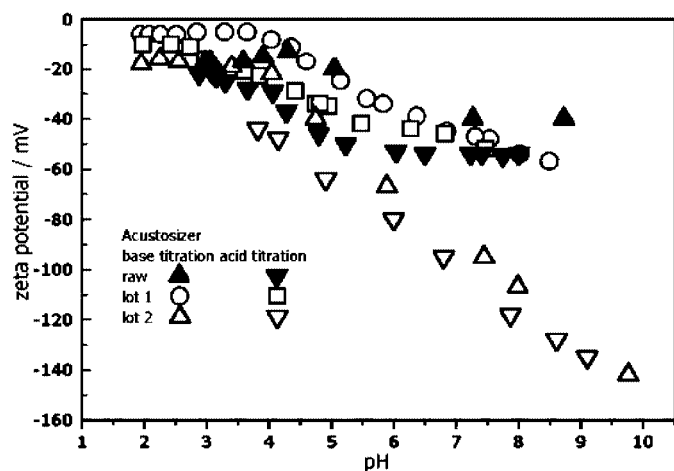


FIG. 1. Hysteresis in the ζ potential of quartz measured by Acustosizer at ionic strength of 0.01 mol dm^{-3} .

cations (23). Figure 1 shows that different time and conditions of acid washing of the same original quartz sample lead to materials having different electrokinetic properties. However, the results obtained with washed and unwashed quartz in the most acidic range are rather consistent, thus, the Al_2O_3 , Fe_2O_3 , CaO , and MgO impurities (mass fraction on the order of 0.1%) are probably not crucial in the problem of existence/nonexistence of the IEP of quartz. Figure 1 shows only negative ζ potentials, which are pH independent over the pH range 2–3, and this suggests that quartz does not have any IEP.

Figures 2–5 show only results obtained for washed quartz (lot 1). Figure 2 shows the surface charge density of washed quartz as the function of the pH and ionic strength. In terms of the shape of the potentiometric curves and the absolute values of the surface charge density, quartz resembles amorphous silica (2, 23).

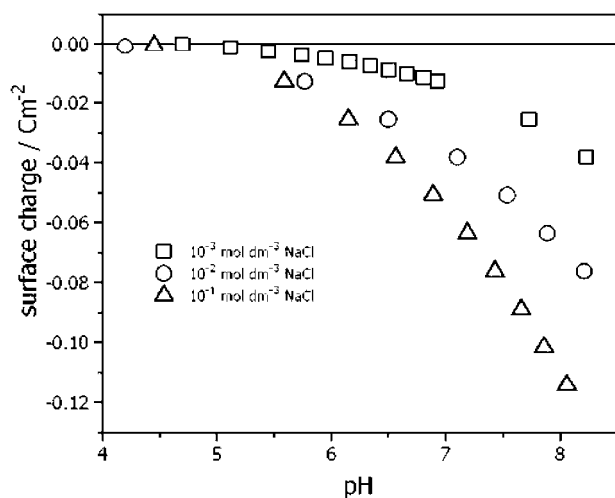


FIG. 2. Surface charge density of quartz as the function of pH and ionic strength.

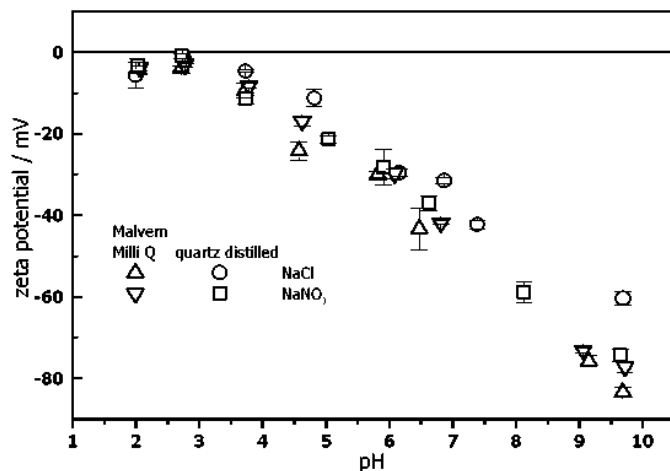


FIG. 3. The ζ potential of quartz in 0.01 mol dm^{-3} NaCl and NaNO_3 in MilliQ water and quartz distilled water measured by Zeta Sizer 3000 (Malvern). Error bars correspond to ± 1 standard deviation.

Figures 3 (Malvern) and 4 (Pen Kem) show that the effect of the nature of the anion (chloride vs nitrate) on the one hand and of the source of water on the other on the electrokinetic behavior of quartz is rather insignificant. While Malvern produced only negative ζ potentials, the ζ potentials at pH about 2 obtained by means of Pen Kem are positive, and they indicate an IEP at pH about 2. However, the absolute values of the positive ζ potentials obtained by means of Pen Kem do not exceed 1 mV, and they are often lower than the standard deviation. Thus the existence of IEP cannot positively be stated.

Figure 5 shows representative results for all five instruments. Base titrations are shown for Acustosizer, DT 1200 and Delsa. Figure 5 indicates relatively consistent ζ potentials of quartz obtained by means of different instruments at $\text{pH} > 4$, and discrepancies at $\text{pH} < 4$ (see Figs. 1, 3, and 4 for more clear picture

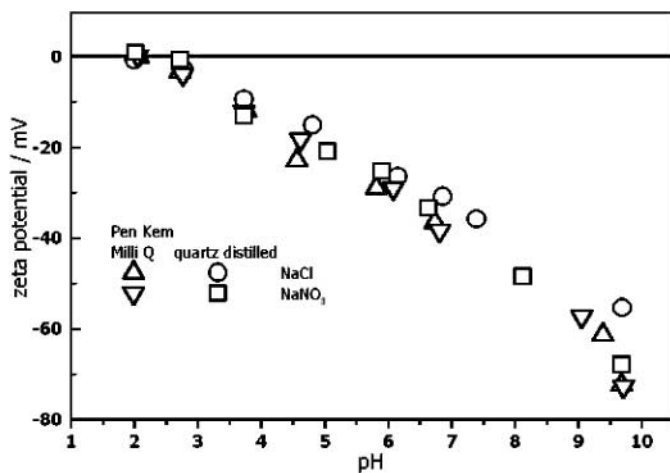


FIG. 4. The ζ potential of quartz in 0.01 mol dm^{-3} NaCl and NaNO_3 in MilliQ water and quartz distilled water measured by Pen Kem Zeemeter 501.

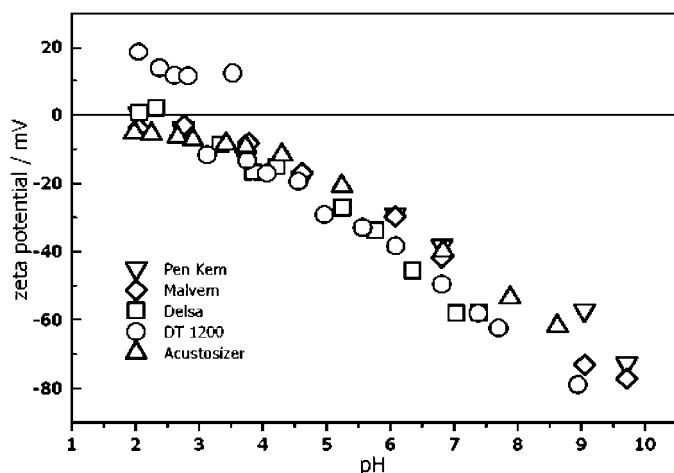


FIG. 5. The ζ potential of quartz measured by five different instruments at ionic strength of 0.01 mol dm^{-3} .

over the pH range where the symbols representing different instruments overlap). The apparent IEP of quartz falls at pH about 3 (DT 1200), 2.5 (Delsa), 2 (Pen Kem), and the measurements performed by means of Malvern and Acustosizer suggest IEP at $\text{pH} < 2$ if any. Among ≈ 100 data points collected by Acustosizer at $\text{pH} < 3$ (a few representative results are shown in Fig. 1) there is no single positive ζ potential. In contrast all ζ potentials measured by DT 1200 at $\text{pH} < 2.5$ were positive!

This sequence is similar to the apparent IEP of fumed silica (2): 4 (DT 1200, Acustosizer, Delsa), 2 (Pen Kem), < 2 if any (Malvern). Comparison of these two sets of apparent IEP suggests that DT 1200 and Delsa tend to produce more positive ζ potentials of silicas in the acidic range than the other instruments and Malvern tends to produce more negative ζ potentials than the other instruments. The ζ potentials obtained by means of Pen Kem are about the average, and Acustosizer produced the most negative ζ potentials of quartz, and results about the average for fumed silica. The above discussed small divergence in the instrument sequence may be due to the difference in the particle shape and size between quartz and fumed silica. Our observation that DT 1200 and Delsa produce more positive ζ potentials of silica in the acidic range than the other instruments is consistent for quartz and fumed silica, but the attempts to find publications reporting ζ potentials of quartz obtained by DT 1200 or Delsa were unsuccessful. Delsa produced a surprisingly high IEP of Stöber silica (24, 25), and this is in line with the present results. The observation that Malvern zetameter gives more negative ζ potentials of silica in the acidic range than the other instruments is consistent for quartz and fumed silica and two of three published electrokinetic studies performed by means of Malvern zetameter also do not support existence of IEP for quartz (Table 1). Bauer *et al.* (20) found one of the highest IEP ever reported for quartz, but they used Malvern Zeta Master, while the Zetasizer 3000 model was used in the present

study. It remains an open question if the ζ potentials obtained by means of DT 1200 and Delsa are overestimated (too positive) or rather the ζ potentials obtained by means of Malvern are underestimated (too negative), but at least one of these alternatives is true. The reason why certain zetameters systematically produce higher IEP of silica in the acidic range than the other is not apparent. These discrepancies may be due to insufficient resistance of certain parts of the instrument, which are brought in contact with the dispersion during the measurement, against corrosion and leaching in strongly acidic media.

The above discussed discrepancies between different instruments complicate the comparison between the IEP of quartz and fumed silica in the present multiinstrument study, but such a comparison is also more reliable than in a single-instrument study. Among the five instruments used in this study, three instruments (DT 1200, Delsa, Acustosizer) suggest that the IEP of fumed silica is higher than the IEP of quartz by at least one pH unit. Two other instruments (Pen Kem, Malvern) gave similar IEP for the both materials. No instrument gave the IEP of fumed silica lower than the IEP of quartz.

Pen Kem and Malvern, the two zetameters which gave matching IEP for two types of silica were used at relatively low solid to liquid ratio, and the equilibration time before taking each data point was long. Combination of these two factors promotes formation of similar surface layers on the original surfaces of fumed silica on the one hand and quartz on the other, as the result of multiple cycles of dissolution/precipitation. With shorter equilibration times and/or higher solid to liquid ratio, the original surfaces of fumed silica on the one hand and quartz on the other, to higher degree maintain their individual characters, and have different IEP. More systematic studies of the effect of the combination of the time of aging and the solid to liquid ratio are necessary to verify the above hypothesis postulating convergence of the electrokinetic potentials of different silicas.

The above discussed instrument artifacts can also be responsible for the apparent shifts in the IEP of silica to high pH induced by potassium, rubidium, and cesium (23). Most publications reporting ζ potentials of silica in 0.1 mol dm^{-3} solutions of potassium, rubidium, and cesium salts suggest the IEP at pH 4–5, while the IEP of the same sample in 0.1 mol dm^{-3} solutions of sodium and lithium salts or at lower ionic strengths falls at substantially lower pH, often beyond the experimental range (or does not exist at all). In view of the present results the apparent IEP of silica measured by means of Malvern falls at lower pH than the apparent IEP measured by means of other instruments, and similar instrument effects on the IEP in 0.1 mol dm^{-3} solutions of potassium, rubidium, and cesium salts can be also expected. Indeed, the ζ potentials of quartz in 0.1 mol dm^{-3} KCl measured by means of Malvern were negative over the entire studied pH range (2–8). This result contradicts most electrokinetic studies of silica in 0.1 mol dm^{-3} KCl, and it indicates that the exact position and even existence/nonexistence of IEP of silica at high concentration of potassium, rubidium, and cesium salts is also sensitive to the instrument artifacts.

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