

more expanded as the *n*-alkane solubility in the micelle decreases, whereas the direct opposite is implied for the other organic liquids. As the organic liquid solubilities in the micelle decrease, the micelle-water interface would be less expanded.

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Acid-Base Properties of Quartz Suspensions¹

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Narrow particle-size fractions of quartz, vitreous silica, and flint $<20\ \mu$, prepared by elutriation, were titrated back and forth several times with NaOH and HCl in the pH range 3–11. The titration curves of quartz were S shaped and showed hysteresis. It was shown that the major part of the protolysis capacity in the alkaline region was caused by silicic acid dissolving during titration. The protolysis capacity in the pH range 3–5 was unexpectedly high. It was shown to be due to a small iron impurity (0.03% Fe). The major part of the protolysis capacity in the range 5–9 was shown to be due to the quartz surface as such. The surface density of acid sites in the whole pH range 3–11 was estimated to 2.6 acid sites/100 Å². As the protolysis capacity of HF-washed quartz was much lower than that of untreated quartz, it was concluded that the latter had a reactive surface layer different from that of the perfect crystal. Titration curves of vitreous silica were similar to those of quartz. The protolysis capacity of flint was higher than that of quartz and vitreous silica but increased only slightly with decreasing particle size. Hence it was concluded that flint has some kind of protolytically reactive inner surfaces in addition to outer surfaces. This was substantiated by X-ray investigation.

Introduction

It is reasonable to assume that the acid-base properties of suspensions of quartz and vitreous silica are confined to outer particle surfaces. If the acid-base sites are equally distributed over all surfaces, the protolysis capacity² must be proportional to the specific surface area of the particles. This assumption has, however, never been proved. It may also be assumed that suspended particles can both split off hydrogen ions instantaneously and reversibly and neutralize base at a slow rate; *i.e.*, they may exert “manifest” as well as “latent” acidity, in the terms of Bjerrum.³

The manifest acidity is assumed to be caused by ionization of hydrogen ions from surface hydroxyl groups. The nature and properties of these groups have been discussed by Boehm.⁴ On amorphous silica,

(1) Taken in part from an unpublished thesis submitted by S. S. J. to the Veterinary and Agricultural College in partial fulfillment of the requirements for the L. Agro. degree.

(2) By “protolysis capacity” is understood equivalents of acid or base consumed in titration of 100 g of powder between definite pH values.

(3) N. Bjerrum, “Selected Papers,” Ejnar Munksgaard, Copenhagen, Denmark, 1949, p 286.

(4) H. P. Boehm, *Angew. Chem.*, **78**, 617 (1966); *Angew. Chem. Intern. Ed. Engl.*, **5**, 533 (1966).

hydroxyl densities ranging from 2 to 5 OH/100 Å² have been found by various methods.⁴ From structural considerations, Stöber⁵ calculated a surface hydroxyl density of about 5 OH/100 Å² on crushed quartz. Experimentally (thermal dehydration), he estimated a density of about 3.6 OH/100 Å².

The latent acidity is attributed to the acid-base properties of silicic acid formed by dissolution. Concentrations of monosilicic acid in "equilibrium" with different forms of amorphous silica have been found to lie within the range of 110–140 mg of SiO₂/l. in acid and neutral solutions at room temperature.^{6–9} The solubility of quartz in water at 25° has been estimated to about 10 mg of SiO₂/l. by extrapolation from high-temperature experiments.^{10,11} In alkaline solutions the solubility of silica is much larger than in acid and neutral solutions due to ionization of silicic acid.⁶

The dissolution of silica is slow, but only in the case of HF-washed quartz is it too slow to be recognized in titration curves of suspensions. It was noted by Holt and King^{12a} that in water, silica dissolves rapidly at first, and later much more slowly. This has also been found by one of us^{12b} in the case of precipitated amorphous silica. The dissolution rate increases with increasing alkalinity. It is therefore not possible to titrate the manifest acidity of any kind of silica without also titrating a part of the latent acidity. The combination of the two kinds of acidity causes the shape of a titration curve to depend on titration velocity. It also gives rise to hysteresis when a base-titrated suspension is titrated back with acid.

In the present investigation, protolysis capacities of four particle-size fractions <20 μ have been compared with specific surface areas calculated from sedimentation analysis. In the case of quartz, a semiquantitative separation of the manifest and the latent acidity has also been made.

Experimental Section

Samples. Quartz is an already powdered sample, 99% α quartz as shown by X-ray diffractometry. After volatilization with HF + H₂SO₄, 0.3% was left. In this residue aluminum and iron were detected. By boiling the fraction <2 μ with 4 N HCl, 0.03% Fe was brought into solution. The iron may originate from steel balls used for crushing the quartz. Its presence caused some trouble in the evaluation of titration curves as will be shown later. Unless otherwise stated, the iron impurity was not removed before titration.

Vitreous silica is clear "Vitresil," completely amorphous to X-rays and completely volatile with HF + H₂SO₄.

Flint is a dark, Senonian specimen, uniform and free

from calcium carbonate. By the X-ray diffractometry methods of Jensen, *et al.*,¹³ the flint was compared with standard quartz (Riedel-de Haën). The area of the 10 $\bar{1}$ 1 quartz peak was 90% that of the standard. By comparing the half-width of the same peak with that of the standard quartz, an average crystal size of 312 Å was estimated. After volatilization with HF + H₂SO₄, 0.3% was left.

Vitreous silica and flint were crushed in a steel mortar and then ground under methanol in a boron-carbide mortar. The powdered samples were separated at 20, 10, 4, and 2 μ by elutriation in 0.002 M sodium pyrophosphate by the method of Jensen and Hansen.¹⁴ After elutriation, the fractions >2 μ were washed three times with water and dried at 110°. The particles <2 μ were flocculated by sodium chloride, washed Cl-free, and dried at 110°. On the quartz fractions 4–10, 2–4, and <2 μ, sedimentation analyses were carried out. Assuming spherical particles, the following specific surfaces were calculated from the size distributions found: 4–10 μ, 0.385; 2–4 μ, 0.93; and <2 μ, 3.16 m²/g.

Cation-exchange capacities of the fractions <2 μ were determined by means of sodium ions at pH 7.65 as described by Jackson.¹⁵ The following values were found: quartz, 4.9; flint, 6.3; and vitreous silica, 5.5 mequiv/100 g.

Titration Experiments. Acid-base titrations were performed by means of a Radiometer "Titrigraph." Powder (0.10–1.00 g) was suspended in 10 ml of de-ionized water or 1 M NaCl, titrated with 0.100 N HCl, and back-titrated with 0.100 N NaOH (carbonate-free). Suspensions were titrated back and forth several times. Titrations were either performed in the same liquid throughout or the suspension was centrifuged and the particles suspended in water after the first

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(12) (a) P. F. Holt and D. T. King, *J. Chem. Soc.*, 773 (1955); (b) S. S. Jørgensen, to be published.

(13) A. T. Jensen, C. J. Wøhlk, K. Drenck, and E. K. Andersen, *Danish Natl. Inst. Bldg. Res. Acad. Tech. Sci. Comm. Alkali Reactions Concrete, Progr. Rept.*, **D1**, 37 (1957).

(14) E. Jensen and H. M. Hansen, *Soil Sci.*, **92**, 94 (1961).

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base titration and after the following titrations. The centrifuged-off liquids were also titrated. During titration, the suspensions were vigorously stirred and CO_2 -free air was bubbled through them. The instrument was equipped with two syringe burets (capacity 0.500 ml each) which could be used alternately so that back-titration with base could be performed immediately after titration with acid, and *vice versa*. Titrations were performed at 20–22°. Unless otherwise stated, a titration pH 3–11 took 10–15 min.

All titration curves were graphically corrected for the protolysis capacity of the solvent. For this correction were used titration curves for HCl titrated with NaOH the same day and under the same conditions as the suspensions. As the protolysis capacity of the solvent is rather large at low and high pH values, the capacity of the suspended mineral is not very accurately determined in these pH ranges. Titration curves are designated in the following way: I, titration with 0.100 *N* HCl from the initial pH to pH 3; II, subsequent titration with 0.100 *N* NaOH from pH 3 to pH 11; and III–V, subsequent titrations with acid, base, and acid pH 3–11.

Results

Quartz. From the curves of Figure 1 it is seen that the particles show buffer effect in the whole pH range investigated. A closer examination of the original curves indicated that the particles have a rather large protolysis capacity above pH 11, but only a very small one below pH 3. The corrected titration curves are in most cases S shaped and hysteresis effects are pronounced, especially in the most acid and the most alkaline regions. The protolysis capacity in the whole range 3–11 increases from one titration to the next, independent of the titrant used. (See Table I.)

The protolysis capacity of 0.50 g is larger than that of 1.00 g titrated in the same volume, this being more pronounced in the alkaline range. The capacity in the alkaline range also increases with increasing titration time. In the alkaline range, the protolysis capacity is greater in NaCl solution and the bending of the curve begins at a lower pH than in water. In titrations in NaCl solution, distinct buffer ranges between pH 4 and 5 are noticed in the base titrations but not in the acid titrations.

The titration curves can be divided into three parts, the two flat parts with pronounced hysteresis, pH 3–5 and pH 9–11, and the steep part with very little hysteresis, pH 5–9. In Table II the protolysis capacity in each part is expressed as acid sites/100 Å^2 using the estimates of specific surface given above.

In the pH range 5–9, the protolysis capacity increases

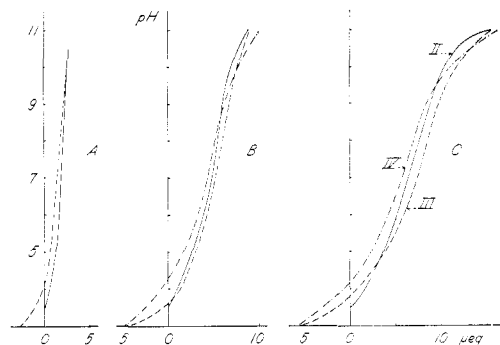


Figure 1. Corrected titration curves of quartz in water. Same liquid throughout: A, 1.00 g, 4–10 μ ; B, 1.00 g, 2–4 μ ; C, 0.50 g, <2 μ : —, titration II; ---, titration III; — · —, titration IV.

slightly from one titration to the next, independent of the titrant. The titrant consumption per 100 Å^2 of different particle-size fractions is approximately the same. The average value from all titrations of the suspensions, 1.00 g, 4–10 μ ; 1.00 g, 2–4 μ ; and 0.50 g, <2 μ , titrated in the normal way in water, is 2.3 acid sites/100 Å^2 . The protolysis capacity in the pH range 3–5 is unexpectedly high. In the search for an explanation the iron impurity was found.

In Figure 2 are shown titration curves of quartz <2 μ from which the iron had been removed by boiling with HCl and washing with deionized water. In these titrations the protolysis capacity in the acid range was much smaller both in water and in 1 *M* NaCl than in the titrations of untreated quartz.

In Figures 3 and 4 are shown titration curves of quartz suspended in pure water after titrations II–IV. The protolysis capacity of the particles in the pH

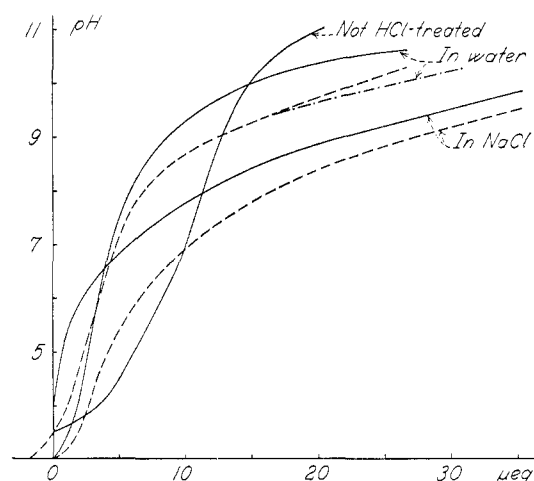


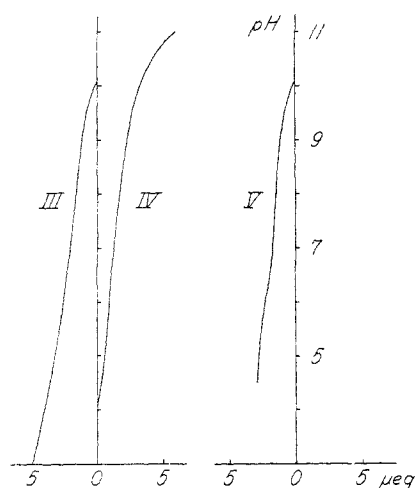
Figure 2. Corrected titration curves of 1.00 g of HCl-treated quartz, <2 μ . Same liquid throughout. Signatures as in Figure 1.

Table I: Titration of Quartz Suspensions. Same Liquid Throughout. Acid-Base Properties in the pH Range 3-11

	Initial pH	Acid/base consumption (cor) mequiv/100 g in titrations			
		I	II	III	IV
1.00 g, 10-20 μ , in water	5.65	...	0.17	0.32	...
1.00 g, 4-10 μ , in water	5.30	0.06	0.27	0.56	...
1.00 g, 2-4 μ , in water	6.02	0.38	0.95	1.35	1.48
0.50 g, <2 μ , in water	7.10	0.50	3.13	4.40	4.45
1.00 g, <2 μ , in water	6.93	1.25	2.05	2.65	...
1.00 g, <2 μ , in water, 1.5 hr	6.85	0.91	3.50
1.00 g, 2-4 μ , in 1 M NaCl	4.62	0.16	1.35	1.75	1.90

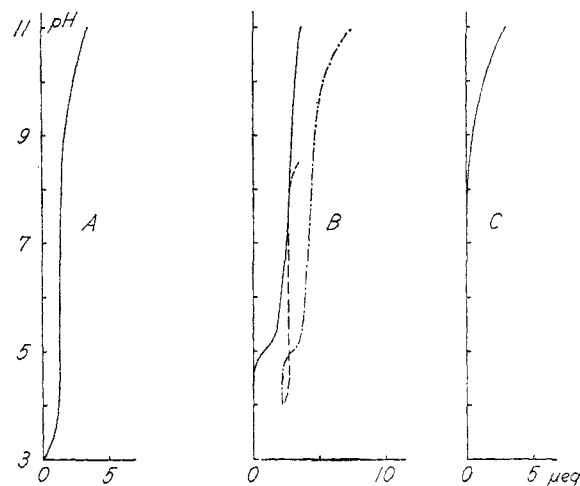
Table II: Protolysis Capacity of Quartz Suspensions in Relation to Estimated Surface Areas

	Acid sites/100 A ²								
	pH 3-5			pH 5-9			pH 9-11		
	II	III	IV	II	III	IV	II	III	IV
1.00 g, 4-10 μ , in water	1.9	5.9	...	1.7	2.5	...	0.6	0.5	...
1.00 g, 2-4 μ , in water	1.7	4.9	4.2	2.3	2.6	2.8	2.2	1.3	2.5
0.50 g, <2 μ , in water	1.4	3.6	3.1	1.9	2.3	2.3	2.6	2.5	3.1
1.00 g, <2 μ , in water	1.1	2.6	...	1.3	1.3	...	1.5	1.1	...
1.00 g, <2 μ , in water, 1.5 hr	0.8 (?)	1.6	4.3
1.00 g, 2-4 μ , in 1 M NaCl	1.3	3.4	2.7	3.2	3.6	3.8	4.3	4.3	5.8

**Figure 3.** Corrected titration curves of 1.00 g of quartz, 2-4 μ , in water. Liquid centrifuged off and particles suspended in fresh water after each titration.

range 5-9 is equivalent to 1.3 acid sites/100 A². In the alkaline range, all the particle suspensions and all the liquids have a high protolysis capacity. In the acid range (pH 3-5), the protolysis capacity is "brought into solution" during titrations.

In the titration of quartz from which a surface layer of approximately 1100 A had been removed by treatment with HF, the protolysis capacity in titration II was about 40% of that of untreated quartz. In subsequent

**Figure 4.** Corrected titration curves of centrifuged-off liquids: A, after titration II; B, after titration III; C, after titration IV; —, base titration (in the cases A and C after acid titration and removal of absorbed CO₂); ---, back-titration with acid; — · —, subsequent base titration.

titrations of suspensions and centrifuged-off liquids there was no significant acid or base consumption.

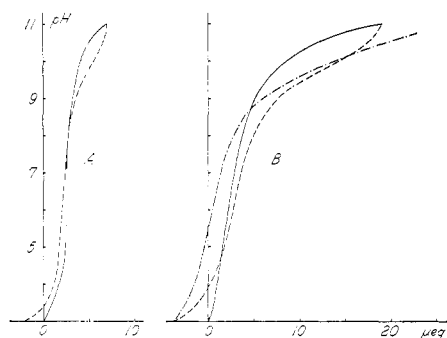
Vitreous Silica. Titration data are given in Table III and Figure 5. Protolysis capacities are of the same magnitude as those of the corresponding quartz fractions, and the curves are very similar to those of HCl-treated quartz. The only appreciable difference is found in the most alkaline range, where the acid

Table III: Titration of Suspensions of Vitreous Silica. Same Liquid Throughout. Acid-Base Properties in the pH Range 3-11

	Initial pH	Acid-base consumption (cor) mequiv/100 g in titrations			
		I	II	III	IV
1.00 g, 11.7-23.4 μ , in water	5.30	Not detectable			
1.00 g, 4.7-11.7 μ , in water	5.17	0	0.29
1.00 g, 2.34-4.7 μ , in water	5.10	0	0.70	0.90	...
0.75 g, <2.34 μ , in water	5.88	0.12	2.53	3.05	3.60 ^a
1.00 g, 2.34-4.7 μ , in 1 M NaCl	5.33	0	1.00	1.53	1.80

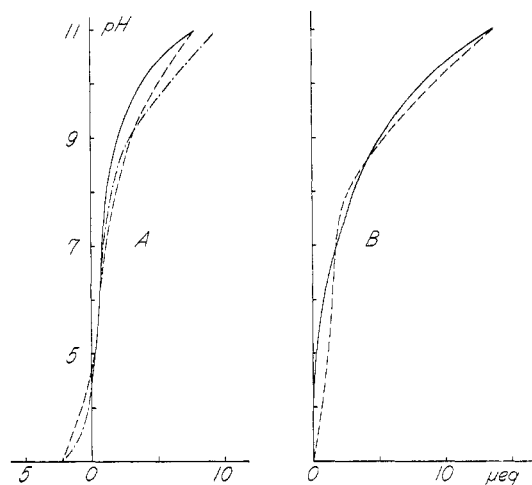
^a Titrated to pH 10.7 only.**Table IV:** Titration of Suspensions of Flint. Same Liquid Throughout. Acid-Base Properties in the pH Range 3-11

	Initial pH	Acid-base consumption (cor) mequiv/100 g in titrations			
		I	II	III	IV
1.00 g, 10.2-20.3 μ , in water	6.08	0.14	2.25	2.62	...
0.30 g, 4.1-10.2 μ , in water	4.85	0.30	2.30	3.16	3.50
0.15 g, 2.03-4.1 μ , in water	5.04	0.67	2.40	5.00	...
0.15 g, <2.03 μ , in water	5.78	0.73	5.16	6.60	7.26
0.15 g, 2.03-4.1 μ , in water, 1.5 hr	6.12	0.40	5.33
0.15 g, 2.03-4.1 μ , in 1 M NaCl	5.28	0	9.0	9.0	...

**Figure 5.** Corrected titration curves of vitreous silica in water: Same liquid throughout: A, 1.00 g, 2.34-4.7 μ ; B, 0.75 g, <2.34 μ . Signatures as in Figure 1.

titration curves of vitreous silica have an inflection point with maximum buffer capacity just below pH 10. In the titrations in NaCl solution, this inflection is also seen in the base titrations.

Flint. Titration data are given in Table IV and Figure 6. The protolysis capacity of this flint is much larger than those of the corresponding quartz and vitreous silica fractions and there is only a small increase in protolysis capacity with decreasing particle size. The general shape of the titration curves of different fractions is the same, but there are smaller differences between the curves obtained in water and 1 M NaCl than in the case of quartz and vitreous silica. In all flint titrations, the protolysis capacity in the

**Figure 6.** Corrected titration curves of flint. Same liquid throughout: A, 0.15 g, <2.03 μ , in water; B, 0.15 g, 2.03-4.1 μ , in 1 M NaCl. Signatures as in Figure 1.

acid range was low; in titration II there was no base consumption at all below pH 4.5.

Discussion

The protolysis capacity of quartz and of vitreous silica was shown to be confined to outer particle surfaces. The flint titrations indicated the presence of some kind of inner surfaces too. From X-ray line broadening, the total specific surface of the crystals is estimated to

be 70 m²/g, which is 22 times that of the finest quartz fraction. This whole surface cannot be accessible to the solution in these fast titrations. The protolysis capacity is at most only nine times that of the corresponding quartz fraction. The smaller the particles, however, the greater the part of the inner surfaces coming into contact with the solution. This explains the increase in protolysis capacity with decreasing particle size.

The protolysis capacity of quartz is due partly to the surface as such and partly to material dissolving during titration. If the titration curve of the surface as such is linear in the whole pH range 3–11 with the same slope as in the range 5–9, the density of acid sites on the surface is 2.6/100 Å². This figure, which is within the range of surface hydroxyl densities found on silica, is only a rough estimate. The particles are not spherical as assumed in the calculation of specific surface areas, and the protolysis capacity of the surface might be larger in the alkaline range.¹⁶

The major part of the protolysis capacity in the alkaline range is assumed to be due to dissolution of the surface layer as monosilicic acid, H₄SiO₄. The titrated solutions are very far from saturation, both with respect to amorphous silica and quartz. Therefore, the dissolution is going on during all titrations. The protolysis capacity in the pH range 3–5 was ascribed to the iron impurity. This might be present either as iron adsorbed on the quartz surface or as soluble silica-

iron oxide complexes. The existence of such complexes was indicated by the experiments of Hazel, *et al.*¹⁷

From the titrations of HF-treated quartz, it is concluded that the untreated quartz had a surface layer much more reactive toward acids and bases than a "pure" quartz surface. It has been found^{9,10} that crushed quartz has a surface layer a few hundred angstroms thick which is not completely amorphous but has a somewhat "loosened" quartz structure. This layer can be removed by hydrofluoric acid. What has been reported on in the present paper is not the acid-base properties of the surface of a perfect quartz crystal but those of a disturbed quartz surface. This kind of surface might well be much more common in nature than the perfect crystal surface.

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