

The Effect of Chemical and Thermal Treatments on the Buffering Capacity of Phillipsite Tuff

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Abstract

Phillipsite tuff samples from Jebal Aritayn (Jordan) was treated chemically by acid, base, and salt and thermally at 200 and 400 °C. Both treated and untreated phillipsite samples were titrated with HCl and NaOH. The potentiometric titration curves showed that Jordanian phillipsite tuff exists in the base form (pH 8.5) and thus has a remarkable buffering capacity toward H⁺. The effect of chemical and thermal treatments on the buffering capacity of zeolite was studied by employing a simple model. The model enables estimating the pK_a values and the acid sites densities for zeolite samples. Depending on the pK_a values of buffering regions and relative to what was reported in literature, it was concluded that the aluminosilicate sites (>SOH₂⁺ and >SOH, >S = Al or Si) as well as the associated silicates, carbonates and bicarbonates of Al, Mg, Ca, and Fe are responsible for the buffering behavior of phillipsite tuff samples. It was also clear that the buffering capacity of phillipsite tuff was reduced by treatment with salt (NaCl), acid (HCl), and base (NaOH). On the other hand, the buffering capacity of phillipsite tuff was enhanced by thermal treatment at 400 °C.

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Abbreviations

ZW: Jordanian phillipsite tuff washed with distilled water.

ZS: Jordanian phillipsite tuff treated with NaCl.

ZA: Jordanian phillipsite tuff treated with HCl.

ZB: Jordanian phillipsite tuff treated with NaOH.

ZT200: Jordanian phillipsite tuff heated to 200 °C.

ZT400: Jordanian phillipsite tuff heated to 400 °C.

x and *y*: The amounts (mol/g) of zeolite sites in the deprotonated and protonated forms, respectively.

t: The amount of H⁺ (mol/L) added.

K⁺: Acid dissociation constant.

[Site]_{*i*}: Site density (mol/g) of buffering region belongs to *K*⁺.

SSR: The sum of square residual.

1. Introduction

Acidification of Earth's terrestrial and oceanic biospheres is now receiving growing attention. This acidification is due to two anthropogenic sources. The first is land acidification, which is caused by nitric and sulfuric acid. The second is ocean acidification, which is due to storage of CO₂ released by human activities (Turley and Scholes, 2009; Bouwman et al, 2002; Unlu et al., 1999).

As a response to the problem of acidification, scientists have to develop their knowledge about the acid-base properties of natural minerals. One of the most important natural minerals is zeolites group, which has a continuous conjugated network of SiO₄ and AlO₄ tetrahedra. Adjacent tetrahedra are linked at their corners via a common oxygen atom, which result in an inorganic macromolecule with structurally distinct three-dimensional framework (Weitkamp, 2000). Zeolites acidity arises from the substitution of Si⁴⁺ by Al³⁺. This substitution creates a negative charge that requires a proton (or another positive ion: Na⁺, K⁺, Mg²⁺, Ca²⁺, etc.) to be balanced (Chu and Chang, 1985; Stoyanov et al., 2008).

The acid-base properties of zeolites are also very important in determining their catalytic activity (Weitkamp, 2000) and their adsorption behavior toward pollutants (Yousef and El-Eswed, 2009). The satisfactory application of surface complexation models to describe the adsorption of metal ions onto clays and minerals is limited by the availability of information about the surface acid sites density of these materials (Goldberg, 1991, 1995). The acidity of synthetic zeolites has been extensively studied because of its importance in catalysis applications. Numerous techniques have been devoted to the investigation of the nature, strength, and distribution of the acid sites in synthetic zeolites. The methods frequently employed have induced ¹H MAS NMR (Pfeifer et al, 1985), IR analysis of the O-H vibrations and the

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deformation features of probes (Ward, 1976), temperature-programmed desorption of adsorbed basic molecules (Karge and Dondur, 1990; Karge *et al.*, 1991), titration of acid sites in aprotic solvents (Tanabe, 1970) and microcalorimetric measurements of differential heats of adsorption of basic molecules on acid sites (Chen *et al.*, 1992; Jozefowicz *et al.*, 1994). Base like pyridine, ammonia, and *n*-butylamine are commonly used in the characterization of the acidity of catalyst. In the determination of the zeolites acidity it is considered that the basic molecules enter the zeolite channels to react with acid sites and the number of acid sites is calculated from the amount of base required to saturate the surface (Ghosh and Curthoys, 1983). To the best of our knowledge, there is no reported study on the acid–base properties (pK_a and acid sites density) of natural zeolites depending on potentiometric titration with H^+ and OH^- . A mere observation was made by Wingenfelder *et al.* (2005), who concluded from titration of natural zeolite (clinoptilolite) with HNO_3 that zeolite has a buffering capacity.

In the present work, the Jordanian phillipsite tuff was chemically treated with salt (ZS), acid (ZA), and base (ZB) and thermally treated at 200 °C (ZT200) and at 400 °C (ZT400). Both treated (ZS, ZA, ZB, and ZT) and untreated (ZW) zeolites were titrated with HCl and NaOH solutions. A simple model was derived for estimating the acid sites densities ($[sites]_a$) of zeolite samples and their acid dissociation constants (pK_a). Relative to pK_a values reported in literature, the obtained pK_a values of zeolite samples (ZW, ZS, ZA, ZB, ZT200 and ZT400) were assigned and thus the effect of treatment on the buffering capacity was evaluated.

2. Materials and Methods

2.1. Pretreatment of Phillipsite Tuff and Characterization (Yousef and El-Eswed, 2009)

The preparation and characterization of Jordanian phillipsite tuff were reported elsewhere (Yousef and El-Eswed, 2009). Briefly, the phillipsite tuff (from north–east Jordan deposit in Jabal Aritayn area) was crushed using Jaw crusher, homogenized, and sieved to different particle size portions. A sample of the particle size 500–1000 μm was washed twice with distilled water and dried in an oven (Thermo Lab Industries, HO 900D) at 110–120 °C. The XRD pattern of the dried phillipsite tuff showed the characteristic peaks of phillipsite. The chemical composition of this tuff obtained from XRF analysis was SiO₂ 42.01, Al₂O₃ 14.10, Fe₂O₃ 11.34, MnO₂ 0.33, MgO 10.33, CaO 8.42, TiO₂ 2.15, K₂O 0.93, Na₂O 1.92, P₂O₅ 0.43, L.O.I. 8.04 (wt %).

2.2. Phillipsite Tuff Treatment

Three chemically treated samples, i.e. ZS, ZA, and ZB, were prepared by treating the zeolite, pretreated in section 2.1, with a salt (NaCl), an acid (HCl), or a base (NaOH), respectively. The treatment performed by impregnating 2.00 g of zeolite in 1 L of 2 M NaCl (purity 99 %), 0.1 M HCl (purity 33 %), and 0.1 M NaOH (purity 98–99 %). After 1 hour, the solution was decanted and the zeolite was reimpregnated in the same solution for another 1 hour. Then the treated zeolite was filtered off, washed with distilled water, and dried overnight in the oven at 105 °C.

The same procedure was followed to prepare a reference sample (ZW) but in distilled water instead of salt, acid, or base. Furthermore, a thermally treated sample (ZT200 and ZT400) were prepared by heating the zeolite, pretreated in section 2.1, at 200 and 400 °C in a Muffle furnace (Lenton Furnaces, Lenton Thermal Design L.T.D). The salt (NaCl), acid (HCl), and base (NaOH) solutions as well as the heating temperature employed in thermal treatments were chosen to be mild to avoid changes in zeolite framework.

2.3. Potentiometric Titration

The pH titration curves were obtained by means of a pH-meter (Metrohm 744). Two suspensions were prepared from 0.10 g sample of zeolite (ZW, ZS, ZA, ZB, ZT200, and ZT400) and 100.0 mL of distilled water. With continuous stirring, the first suspension was titrated with 0.01 M HCl whereas the second with 0.01 M NaOH at room temperature. As a reference, 100.0 mL distilled water sample (without zeolite) was titrated in a similar manner.

3. Results and Discussion

3.1. Potentiometric Titration

Natural phillipsite tuff samples that were prepared by impregnating the phillipsite tuff in 2 M NaCl salt (ZS), 0.1 M HCl acid (ZA), and 0.1 M NaOH base (ZB) as well as by heating at 200 and 400 °C (ZT200 and ZT400) beside a reference sample (ZW) were studied in the present work. The acidity/basicity of the product was investigated in relation to their potentiometric titration curves with 0.01 M HCl and 0.01 M NaOH as shown in Figure 1. The pH titration curve for distilled water is also given for the purpose of comparison.

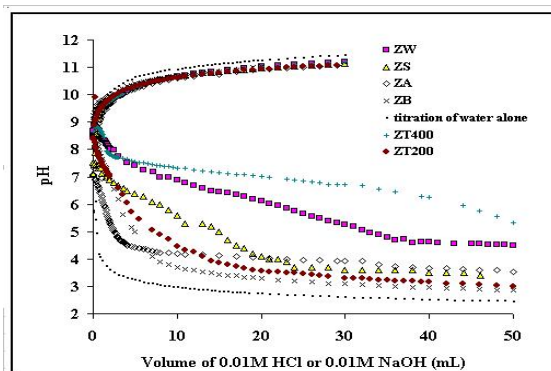


Fig 1. The pH titration curves for water, ZW, ZS, ZA, ZB, ZT200 and ZT400 samples.

The titration curves of water in the presence of zeolite samples have significantly higher pH values when titrated with HCl and very slightly lower pH values when titrated with NaOH relative to the pH titration curve of solid-free water (Figure 1). This indicates that zeolite sites are mainly in the form of salts or conjugate bases so that these sites have higher ability to react with H^+ than with OH^- titrant. This is further supported by the observation that the initial pH at $V_{HCl/NaOH} = 0$ (before titration with acid or base) of zeolite suspensions are higher than 7 (ZW 8.48, ZS 7.5, ZA 7.05, ZB 9.04, ZT200 8.42 and ZT400 8.85). Accordingly, the titration curves with HCl rather than NaOH titrant will be investigated in the present article.

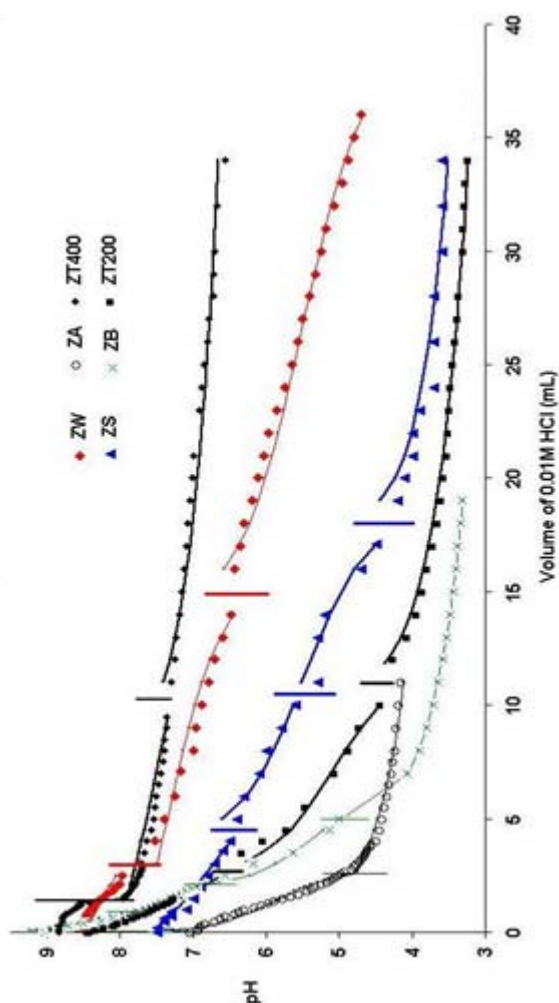


Fig. 2. The results of fitting buffering regions of zeolite samples ZW, ZS, ZA, ZB, ZT200 and ZT400.

3.3. Buffering Capacity

Jordanian phillipsite tuff consists of about 50 % of zeolite and 50 % of non-zeolite content (Al-Rashdan, 2000). The zeolite content is in the form of aluminosilicate ($>\text{SOH}_2^+$, $>\text{SOH}$ and $>\text{SO}^-$, where $>\text{S}$ is Al or Si):



whereas the non-zeolite contents are assumed to be in the form of metal silicates which accounts for olivine, pyroxene and feldspars content of phillipsite tuff. Metal carbonates are also possible because of the calcite content of phillipsite tuff. Metal bicarbonates results during titration of carbonates.

The XRF results of Jordanian phillipsite tuff indicate the presence of significant amounts of Si, Al, Fe, Mg, and Ca relative to Na, K, P, and Mn (see Experimental Part). Brønsted acidity in zeolite is attributed to aluminum substitution. The Si and Al are present in the aluminosilicate zeolite framework, which has a buffering effect (Chu and Chang, 1985; Stoyanov *et al.*, 2008). Aluminum may present in extra-framework (Sokol *et al.*, 2000). The Al, Fe, Mg, and Ca elements may occur in the silicate, carbonate, or bicarbonate forms which also have buffering effects. Accordingly, the phillipsite tuff species that contribute to the buffering capacity are the aluminosilicate framework as well as the Al, Fe, Mg, and Ca silicates, carbonates, and bicarbonates.

The assignment of specific acid/base sites for each buffering region in the zeolite samples (ZW, ZS, ZA, ZB, ZT200, and ZT400) can be attempted by comparing the obtained pK_a values of acid sites of zeolite samples (Table 1) with those reported in literature for both the zeolitic and non-zeolitic components present in phillipsite tuff.

3.3.1. Buffering Capacity of Untreated Zeolite (ZW)

To our knowledge, there is no reported pK_a values for zeolite aluminosilicate framework. The situation is different in clays where there are many reports on potentiometric titration of clays. Such reports lead to estimates, shown in Table 2, for $>\text{SOH}/>\text{SOH}_2^+$ and $>\text{SO}^-/>\text{SOH}$ ($>\text{S}$: Al or Si); average pK_{a1} 5.1 and pK_{a2} 8.4 (equations 6 and 7, Table 2). Furthermore, the reported values using nonelectrostatic interaction approach on clay, which is similar to our approach are pK_{a1} 4.9 and pK_{a2} 8.4 (Lu and Smith, 1996). This leads to the suggestion that the buffering regions of zeolite sample ZW at pK_a 5.6 and pK_a 8.3 (Table 1) are due to aluminosilicate sites.

For pure phillipsite mineral, the Si/Al mol ratio is 1.7 (Baerlocher *et al.*, 2001). The Brønsted acid sites density estimated for phillipsite depending on this Si/Al ratio is 2.70×10^{-3} mol/g (Baerlocher *et al.*, 2001). The phillipsite content of Jordanian phillipsite tuff is about 50 % (Al Rashdan, 2000), thus the Brønsted acid site density of aluminosilicate in phillipsite tuff is expected to be about 1.35×10^{-3} mol/g. This value is close to the site density in sample ZW at $pK_a = 8.3$ (9.9×10^{-4} mol/g, Table 1). The site density for ZW sample at $pK_a = 8.3$ and at $pK_a = 5.6$ should be equal if they are due only to aluminosilicates. Thus, the extra amount of site density at $pK_a = 5.6$ (1.8×10^{-3} mol/g, Table 1) relative to that at $pK_a = 8.3$ (9.9×10^{-4} mol/g, Table 1) is due to non-zeolitic sites of Ca-Mg silicates which have pK_a values in this regions (Table 2, equations 12, 15, 16).

Table 2. The pK_a values and the corresponding equations of compounds of Si, Al, Ca, Mg, and Fe present in clays.^a

Species	Equation (Equation no.)	pK_a	ref
>SOH/>SOH ₂ ⁺ (>S : Al or Si)	>SOH ₂ ⁺ ↔ >SOH + H ⁺ (6)	4.5	b
		6.0, 5.2	c
		4.9, 5.2	d
		average 5.1	
>SO ⁻ />SOH (>S : Al or Si)	>SOH ↔ >SO ⁻ + H ⁺ (7)	7.9	b
		8.6, 8.1	c
		8.4, 7.6	d
		average 8.4	
Al ³⁺ /H ₃ SiO ₄ ⁻ , CO ₃ ²⁻ , HCO ₃ ⁻	Al ³⁺ + H ₄ SiO ₄ ↔ AlH ₃ SiO ₄ ²⁺ + H ⁺ (8)	2.5	e
	2Al ³⁺ + HCO ₃ ⁻ ↔ Al ₂ (OH) ₂ CO ₃ ²⁺ + 3H ⁺ (9)	7.3	e
	3Al ³⁺ + HCO ₃ ⁻ ↔ Al ₃ (OH) ₄ HCO ₃ + 4H ⁺ (10)	9.4	e
Ca ²⁺ /H ₂ SiO ₄ ²⁻ , H ₃ SiO ₄ ⁻ CO ₃ ²⁻ , HCO ₃ ⁻	Ca ²⁺ + H ₃ SiO ₄ ⁻ ↔ CaH ₂ SiO ₄ + H ⁺ (11)	9.8	e
	Ca ²⁺ + H ₄ SiO ₄ ↔ CaH ₃ SiO ₄ ⁺ + H ⁺ (12)	9.1	e
	Ca ²⁺ + HCO ₃ ⁻ ↔ CaCO ₃ + H ⁺ (13)	7.1	e
	Ca ²⁺ + H ₂ CO ₃ ↔ CaHCO ₃ ⁺ + H ⁺ (14)	5.2	e
Mg ²⁺ /H ₂ SiO ₄ ²⁻ , H ₃ SiO ₄ ⁻ CO ₃ ²⁻ , HCO ₃ ⁻	Mg ²⁺ + H ₃ SiO ₄ ⁻ ↔ MgH ₂ SiO ₄ + H ⁺ (15)	8.6	e
	Mg ²⁺ + H ₄ SiO ₄ ↔ MgH ₃ SiO ₄ ⁺ + H ⁺ (16)	8.8	e
	Mg ²⁺ + HCO ₃ ⁻ ↔ MgCO ₃ + H ⁺ (17)	7.4	e
	Mg ²⁺ + H ₂ CO ₃ ↔ MgHCO ₃ ⁺ + H ⁺ (18)	5.3	e
Fe ³⁺ /H ₂ SiO ₄ ²⁻ , H ₃ SiO ₄ ⁻ CO ₃ ²⁻ , HCO ₃ ⁻	Fe ³⁺ + H ₄ SiO ₄ ↔ FeH ₃ SiO ₄ ²⁺ + H ⁺ (19)	0.6	e
	Fe ³⁺ + H ₂ O + CO ₃ ²⁻ ↔ Fe(OH)CO ₃ + H ⁺ (20)	3.8	e
	Fe ³⁺ + 2HCO ₃ ⁻ ↔ Fe(CO ₃) ₂ ⁺ + 2H ⁺ (21)	11.3	e
	Fe(OH) ₃ (21)	5.1	e

From Table 2, the bicarbonates of Ca and Mg, which have pK_a values 5.2 (equation 14) and 5.3 (equation 18) may contribute to the buffering region of ZW sample at pK_a 5.6 (Table 1) in addition to aluminosilicate sites.

The carbonates of Al, Ca, and Mg have pK_a values 7.3, 7.1, and 7.4, respectively (equations 9, 13, and 17). Thus, the buffering regions of ZW sample at pK_a 7.6 (Table 1) can be assigned to Al₂(OH)₂CO₃²⁺, CaCO₃, and MgCO₃.

3.3.2. Buffering Capacity of Treated Zeolites (ZA, ZB, ZS, ZT200 and ZT400)

The buffering regions of treated zeolitic samples ZS, ZA, ZB, ZT200 and ZT400 were assigned according to those of ZW sample. The pK_a values 5.9 (ZA), 5.4 (ZB), 5.5 (ZS), 5.1 (ZT200) and 5.8 (ZT400) are assigned to aluminosilicate and calcium and magnesium bicarbonates and aluminum and iron hydroxides; 7.5 (ZB and ZT400) and 6.8 (ZS) are assigned to calcium, magnesium, and aluminum carbonates; 8.3 (ZB), 8.1 (ZT200) and 8.0 (ZT400) are assigned to aluminosilicate (Table 1).

The buffering regions with pK_a values less than 4 (1.8, 2.4, 2.6 and 3.0, Table 1) are difficult to be assigned because several species resulted during the course of titration may contribute to these regions.

3.4. Effects of Treatment on the Buffering Capacity of Zeolite

On the light of the assignment of treated samples (ZS, ZA, ZB, ZT200 and ZT400), the effect of acid, base, salt, and thermal treatment upon buffering capacity of zeolite can be evaluated.

Acid-treatment of phillipsite tuff using 0.1 M HCl leads to the (i) vanishing of buffering region at pK_a 8.3 (in ZW sample, assigned to >SO⁻) due to the destruction of phillipsite structure, (ii) vanishing of buffering region at pK_a 7.6 (in ZW, assigned to carbonates) due to the neutralization of carbonates of Ca, Mg, and Al, (iii) decrease of site density [Sites]_t at pK_a 5.6 (ZW, assigned to >SOH and bicarbonates of Ca/Mg) due to destruction of phillipsite structure and neutralization of bicarbonates species.

Base-treatment of phillipsite tuff using 0.1 M NaOH leads to (i) a decrease in the site density of the buffering region at pK_a 8.3 (ZW, assigned to >SO⁻) (ii) a decrease of the site density of the buffering region at 7.5 and 5.4. These two observations can be attributed to the ability of sodium ions to substitute Ca and Mg ions in their aluminosilicates and silicates leading to dissolution of these species.

Salt-treatment of phillipsite tuff using 2 M NaCl leads to (i) disappearance of the buffering region at pK_a 8.3 (in ZW sample, assigned to >SO⁻), (ii) decrease of site densities of buffering region at 6.8 (assigned to carbonates) and 5.5 (assigned to >SOH and bicarbonates). This loss of part of the buffering capacity can also be attributed to the ability of sodium ions to substitute Ca and Mg ions in their aluminosilicates, silicates, carbonate, and bicarbonates leading to their dissolution.

Heating phillipsite tuff at 400°C did not affect the sites at pK_a 8.0 (assigned to >SO⁻) and 7.5 (assigned to carbonates), however the sites at pK_a 5.8 (assigned to >SOH and bicarbonates) increased significantly. On the other hand, heating phillipsite tuff at 200°C leads to decrease of the sites at 8.1 (assigned to >SO⁻) and 5.1 (assigned to >SOH and bicarbonates). The carbonates and bicarbonate are reported to be not affected by thermal treatment up to 600 °C (Gunasekaran and Anbalagan, 2007). The effect heating on the XRD pattern of natural phillipsite was reported by Rykl and Pechar (1991). Heating at 200 °C and 500 °C resulted in transforming phillipsite into wairakite and meta-

wairakite, respectively. Wairakite is considered as feldspathoid and has an ion exchange ability which contributes to acid site density. Other XRD studies (Komarneni, 1985; Liguori *et al.*, 2006; Cappelletti *et al.* 2011) indicated that heating phillipsite loaded with cesium, strontium, and chromium at 600-800 °C leads to collapse of the phillipsite structure and formation of metal-feldspar phase.

Thus, the buffering capacity of phillipsite tuff enhances through thermal treatment to 400 °C and reduces by HCl, NaOH, and NaCl-treatments and thermal treatment at 200 °C. According to the sum of total sites ([Sites]_t) at pK^*_a 5.4-5.9, which includes both aluminosilicate and bicarbonate species, the buffering capacity of zeolite samples decreases in the order: ZT400 > ZW > ZS > ZT200 > ZB > ZA.

4. Conclusions

The potentiometric titration curves showed that natural zeolite exists in the salt or base form and thus has a remarkable buffering capacity when titrated with HCl. Both chemical and thermal treatments affect such capacity. Chemical treatment of zeolite with NaCl, HCl, and NaOH and thermal treatment at 200°C decrease the buffering capacity of zeolite whereas heating the zeolite at 400°C enhances its buffering capacity. Natural zeolite which is available in low cost and huge quantities can be used to solve the problem of acidification of soils and aquatic systems.

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