

Task No. 2

SURFACE CHARGE AND POINT OF ZERO CHARGE OF OXIDE ADSORBENTS AND THEIR MIXTURES

I. Task purpose

The purpose of this task is estimation of the point of zero charge and surface charge of silica and alumina oxides and their mixture using the potentiometric titration method.

II. Basic issues

1. Point of zero charge.
2. Isoelectric point.
3. Point of zero charge measurements.
4. SiO₂ and Al₂O₃ materials.

References

1. M. Kosmulski “ *Surface charging and points of zero charge*”, Surfactant science series, vol. 145, CRC Press/Taylor & Francis Group, 2009.
2. M.A.F. Pyman, J.W. Bowden and A.M. Posner, *Clay Minerals*, 14 (1979) 87-92.

Surface charge on natural and synthesized materials can develop in three principal ways:

- as a result of proton or other ion complexation on the particle surface;
- from lattice imperfections on the particle surface;
- from isomorphous ion substitution within the crystal structure.

With regard to synthetic silica and alumina minerals, surface complexation reactions are expected to be a dominant source of surface charge.

Net total particle surface charge, σ_P , is defined quantitatively as the sum of four components:

$$\sigma_P = \sigma_O + \sigma_H + \sigma_{IS} + \sigma_{OS}, \quad (1)$$

where: σ_O is the net permanent structural-charge density due to isomorphous substitutions; σ_H is the net proton surface charge density created by the difference between the moles of protons and hydroxide ions complexed by the surface functional groups; σ_{IS} is the net inner-sphere complex surface charge density resulting from the net total charge of ions (excluding H^+ and OH^-) bound into inner-sphere surface coordination; σ_{OS} is the net outer-sphere complex surface charge density resulting from the net total charge of ions (excluding H^+ and OH^-) bound into outer-sphere surface coordination. If σ_P is non-zero (i.e. the particle possesses charge), then the law of surface charge balance requires that σ_P be balanced by the diffuse layer surface charge density, σ_D , which is equal in magnitude, but opposite in sign to σ_P :

$$\sigma_P = -\sigma_D. \quad (2)$$

Ions in the diffuse layer are subjected to counteracting diffusion and electrostatic gradients such that they move freely in solution but a net diffuse ion swarm charge is sustained in local proximity to the surface, effectively balancing σ_P .

The term *point of zero charge* (PZC) is defined as the conditions at which the surface charge density (Δq) equals zero. Zero net charge density does not imply the absence of any charges, but rather the presence of equal amounts of positive and negative charge.

$$\Delta q = (q_+ - q_-) = \sigma_{IS} + \sigma_{OS} + \sigma_D, \quad (3)$$

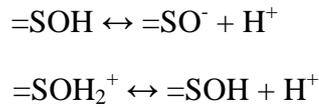
where: q_+ and q_- refer to the adsorbed cation and anion charge, respectively, in units of moles of charge per square meter (C/m^2).

The intrinsic surface charge density, σ_{IN} , represents components of surface charge developed from the mineral structure, which must be balanced by adsorption of ions from solution:

$$\sigma_{IN} = \sigma_O + \sigma_H = -\Delta q. \quad (4)$$

The *point of zero net charge (PZNC)* is defined as the pH value where σ_H is equal to zero. Therefore, using Eqn. 4, this is the pH value where $\Delta q = -\sigma_O$. Experimental methods for measuring surface charge components from Eqn. 4 include proton titration for σ_H , preferential Cs^+ adsorption for σ_O and background ion adsorption for Δq . Whereas σ_O is constant for given material, σ_H and Δq vary with pH and ionic strength.

The value of pH is commonly used to describe PZC for the systems in which H^+/OH^- are the potential determining ions:



When pH is lower than the PZC value, the system is said to be “below the pzc”, where the acidic solution donates more protons than hydroxide groups, and so the adsorbent surface is positively charged. Conversely, above the PZC the surface is negatively charged – see Fig. 1.

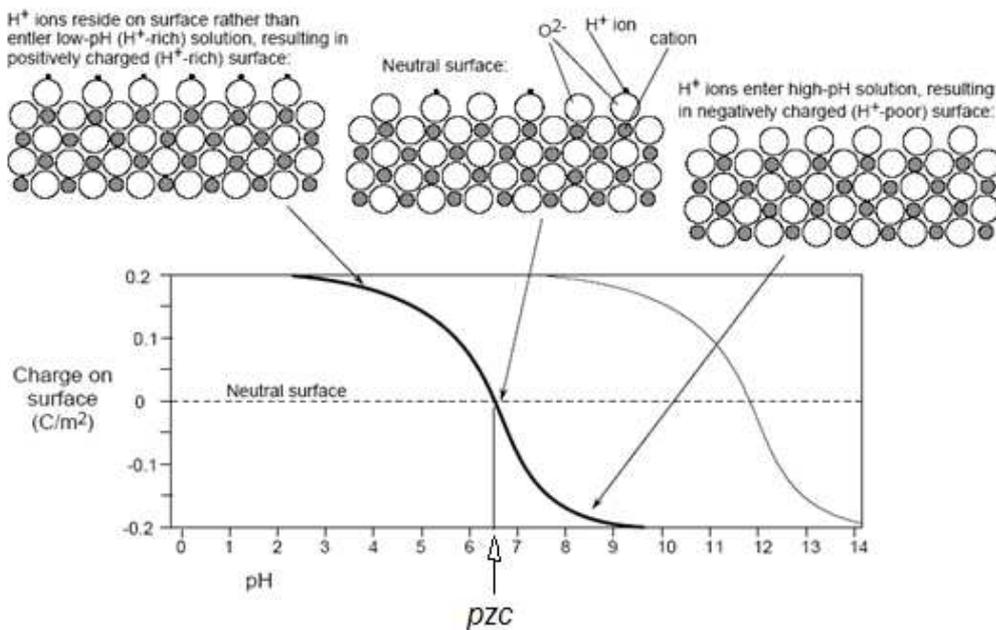
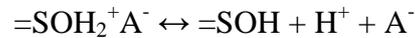
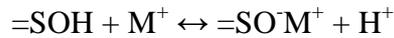


Fig. 1. Schematic representation of the point of zero charge [1].

Point of zero charge is of fundamental importance in surface science and has countless applications in technology of colloids, e.g. flotation of minerals. At PZC the colloidal system exhibits zero zeta potential (particles remain stationary in an electric field), minimum stability (exhibits maximum coagulation/flocculation rate), maximum solubility of the solid phase and maximum viscosity of the dispersion.

Apart from hydrogen ions, background electrolyte ions play a significant role in creating the surface charge. They react with oxide surface hydroxyls creating complex fusions.



The surface charge density is an algebraic sum of charges of groups mentioned above.

$$\sigma_0 = B \cdot \{ =SOH_2^+ + =SOH_2^+A^- - =SO^-M^+ - =SO^- \},$$

where: **B** – the coefficient of conversion from the surface density expressed in mol/m² into the charge density expressed in C/m².

The techniques for the PZC determination are founded on the assumption that protons and hydroxyl groups are potential-determining ions. The pH at which the surface has zero net charge, known as pH_{PZC}, is characteristic of amphoteric surfaces and is determined by the type of surface sites on solids and their structures.

The most frequently used method of the point of zero charge estimation in the metal/electrolyte interface is a potentiometric titration. It consists in pH changes estimation depending on the amount of added acid or base for electrolyte and suspension having the same ion strength. The intersection point of potentiometric titration curves gives the PZC value – see Fig. 2.

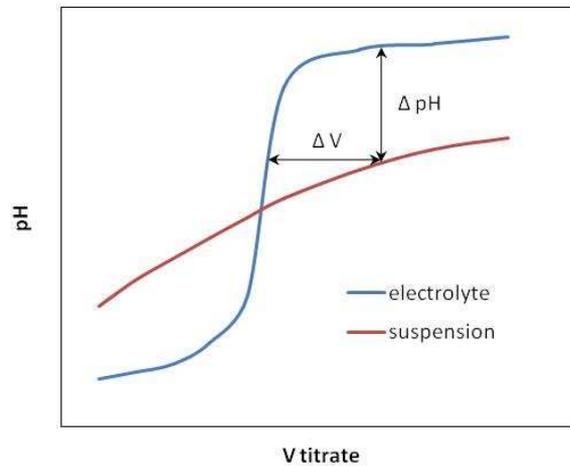


Fig. 2. Curves of titration of the background electrolyte and suspension.

The surface charge density is possible to evaluate from the difference in volumes of added acid or base to obtain appropriate pH value of suspension using the equation:

$$\sigma_0 = \Delta V \cdot c \cdot F / m \cdot S_w \quad (1)$$

where: $\Delta V = (V_s - V_e)$ – the difference in volume of titrate necessary to obtain the appropriate pH value of electrolyte and suspension;

F – the Faraday constant;

c – the concentration of titrate;

S_w – the specific surface area of oxide;

m – the mass of oxide in suspension.

The surface charge density is also possible to obtain by comparison the change in concentration of hydroxyl ions and protons for some volume of acid or base following the equation:

$$\sigma_0 = V_e \cdot (10^{-\text{pH}_e} - 10^{\text{pH}_s} - 10^{-14+\text{pH}_e} + 10^{-14+\text{pH}_s}) / m \cdot S_w \quad (2)$$

where: V_e – the volume of electrolyte;

pH_e – the pH of electrolyte solution;

pH_s – the pH of suspension.

The point of zero charge may be estimated using the suspension effect method (Pallmann effect). It consists in existing various activities of protons measured in the sediment layer and in clear solution above the sediment. Solid possesses the zero charge of surface if the difference between the solution and the sediment does not exist.

$$\Delta \text{pH} = \text{pH}_{\text{zaw}} - \text{pH}_{\text{roztw}} \quad (3)$$

The other methods used for determination of the PZC are:

- common intersection point (CIP) of potentiometric titration curves obtained at three or more ionic strengths (see Fig. 3);
- intersection point of potentiometric titration curves obtained at two ionic strengths;
- the titration curves obtained at different ionic strengths merge below and above a certain pH.

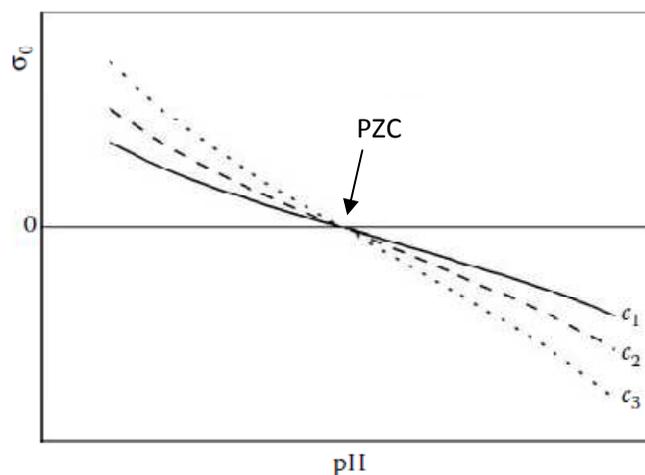


Fig. 3. Common intersection point (cip) of potentiometric titration [2].

The *isoelectric point* (IEP) is defined as the conditions under which the electrokinetic charge density and thus the electrokinetic potential (ζ) equals zero. It is determined by the electrokinetic methods – electrophoresis, electroosmosis as well as electroacoustic method. The pH value of the solid dispersion where the electrokinetic potential of the solid particles is equal to zero is known as pH_{IEP} . Equality between pH_{PZC} and pH_{IEP} exists only if no specific sorption of ions from the solution takes place.

The PZC is affected by the nature of the inert electrolyte and by the temperature – see Table 1. The nature of titrate as well as the rate of titration also affect the PZC value – see Fig. 4.

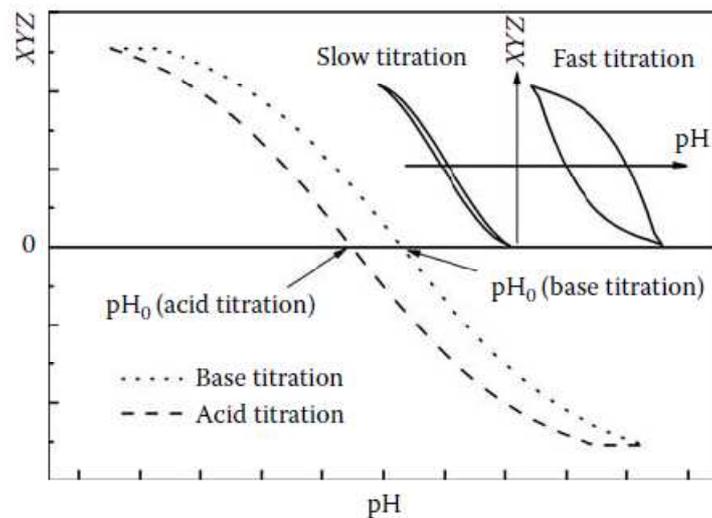


Fig. 4. Influence of titrate and velocity of titration on PZC [2].

Table 1. Experimental PZC values for Al_2O_3 and SiO_2 materials obtained at 25°C by various scientists [3].

Al_2O_3			
Material	Electrolyte	Method	pH
γ , Aerosil, purified	0.001-0.1 M $NaNO_3$	CIP	8.3
Fumed	0.001 M $NaCl$	IEP	9.5
α , CR6	0.001-0.1 M $NaCl$	CIP	8.8
α , Aldrich, heated at 700°C	0.005 M $NaCl$	IEP	6.5
α , 99,99% Showa Denko	0.001 M $NaNO_3$	IEP	9.2

Degusa C	0.005-0.5 KNO ₃	CIP	8.0
SiO₂			
Material	Electrolyte	Method	pH
Fumed	0.001 M NaCl	IEP	2.2
Ludox HS, DuPont	0.001 M KCl	IEP	3.0
From sodium silicate	0.001 M NaCl	IEP	2.3
Quartz, Alfa Aesar	0.001-0.1 M NaNO ₃	CIP	2.9
Quartz, high purity, Bottley	0.001 M KCl	IEP	3.0
Klebosol	0.05 M KCl	IEP	4.0
Stober	0.01 M KNO ₃	IEP	2.9

The PZC of a mechanical mixture of x g alumina and y g silica is expected to be at the pH where the negative charge developed on x_g alumina is equal to the positive charge developed on y_g silica. It exists between the values obtained for pure oxides. In order to calculate the PZC as a function of composition, the titration curves of silica and alumina should be plotted on a charge per g basis. Then the weight percent composition $x/(x+y)$ corresponding to a particular PZC (pH= z) is given at the constant ionic strength by:

$$\{\sigma_{Al} \cdot x/(x+y)\}_{pH=z} + \{\sigma_{Si} \cdot y/(x+y)\}_{pH=z} = 0 \quad (4)$$

$$y/(x+y) = -\sigma_{Si}/(\sigma_{Al} - \sigma_{Si}) \quad (5)$$

where: σ_{Al} and σ_{Si} – the surface charges of alumina and silica oxides at pH= z (expressed in C/g). The calculation can be done for each concentration of inert electrolyte [4].

Silicates are the oxides of silica, where the Si atom shows tetrahedral coordination, with four oxygen atoms surrounding the central Si atom – see Fig. 5.

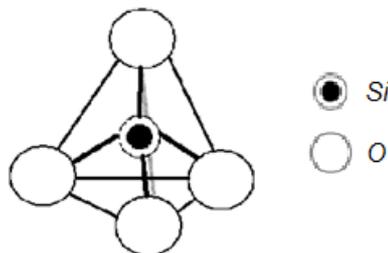


Fig. 5. Tetrahedral structural unit of silica.

In each of the thermodynamically stable forms of silica all of oxygen atoms of the SiO_4 tetrahedra are shared with others, yielding the net chemical formula: SiO_2 . Silicon dioxide has a number of distinct crystalline forms (polymorphs, e.g. quartz, tridimite, cristobalite, faujasite, coesite, stishovite, moganite) in addition to amorphous forms. Silica gels belong to amorphous silicates possessing the non-recurrent network of tetrahedra, where all the oxygen corners connect two neighboring tetrahedra. The amorphous structure of silica is shown in Fig. 6, where for clarity some oxygen atoms behind the plane of the picture or in front of it are omitted.

Silica gel, a porous solid amorphous form of hydrous silicon dioxide, has the nominal chemical formula of $\text{SiO}_2 \cdot x\text{H}_2\text{O}$. It is constituted by randomly linked spheroidal polymerized silicate particles – the primary particles. The properties of silica gels are a result of the state of aggregation of the primary particles and the chemistry of their surfaces. The surface area, porosity and surface chemistry can be controlled during the production process.

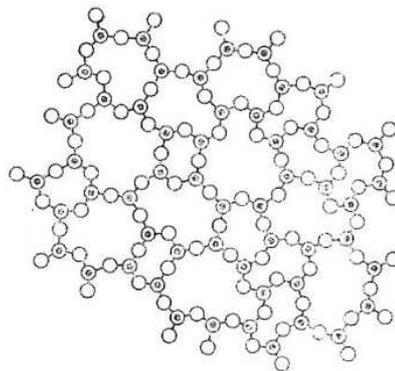
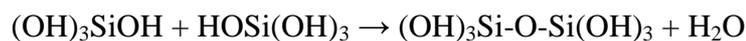


Fig. 6. The amorphous structure of silica gel [5].

Silica gels are fabricated in the sol-gel process as a result of polycondensation of orthosilicic acid:



This reaction leads to obtaining macroparticles of silicic acid. It proceeds in three stages:

- Polymerization of monomers to form small primary particles;
- Growth of primary particles;
- Linking of particles into branched chains, networks and finally gel.

As a result, the silica particles covered by the SiOH groups are obtained. Forms of created hydroxyl groups are collected in Fig. 7.

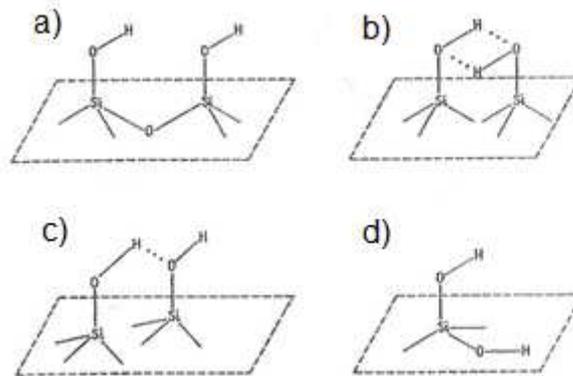


Fig. 7. Forms of hydroxyl groups on the surface of silica gel: a) single (isolated); b) hydrogen bonded; c) active; d) double (germinal) [5].

Structure characterization of amorphous silica gel Si-100 obtained using the low temperature nitrogen adsorption/desorption is presented in Fig. 8.

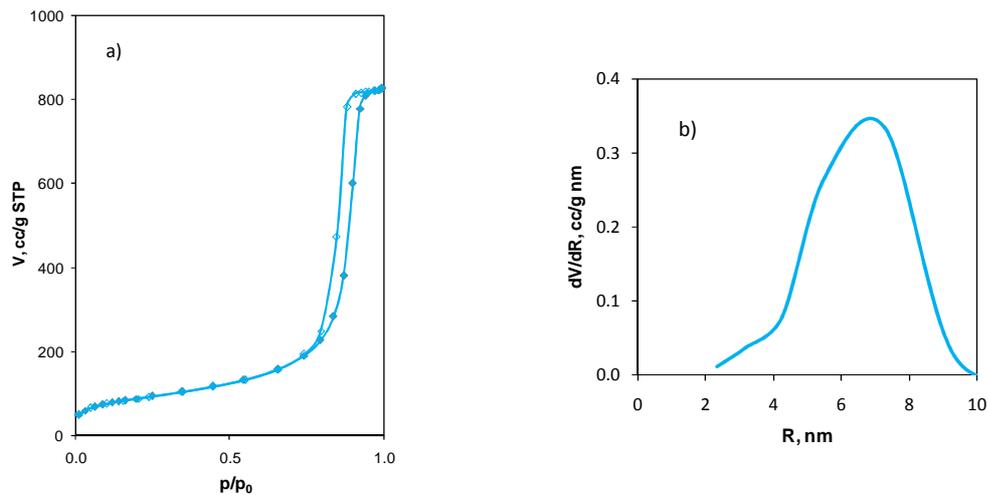


Fig. 8. Nitrogen adsorption/desorption isotherm (a) and pore size distribution (b) for Si-100 silica.

Alumina (Al_2O_3) are mainly obtained by dehydration of various aluminum hydroxides, e.g bohemite. Boehmite structure and decomposition impose a path, kinetically favoured toward α -alumina, the thermodynamically stable form of aluminum oxide, via the sequence of metastable transition aluminum oxides:



The first systematic classification of alumina was proposed by Ginsberg and was subsequently modified by Lippens. It is based on the temperature ranges in which alumina is obtained from hydroxides. Group γ comprises low-temperature aluminum oxides ($\text{Al}_2\text{O}_3 \cdot x \text{H}_2\text{O}$, where: $x = 0$ to 0.6) obtained at temperatures below 600°C. This group includes ρ -, χ -, η - and γ -aluminum oxides. Group δ encompasses high-temperature aluminum oxides (practically anhydrous Al_2O_3) obtained in the temperature range from 900°C to 1000°C. This group includes κ -, θ - and δ -aluminum oxides. At a temperature 1200°C and higher α -alumina oxide is obtained.

The form of alumina most commonly used as an adsorbent is γ - Al_2O_3 , with the specific surface area of 100-200 m^2/g . Their surface is built of O^{2-} and Al^{3+} ions, with only $\frac{3}{4}$ of the positions specific for aluminum being occupied, the balance constituting surface defects (vacancies).

Alumina may contain different quantities of surface hydroxyls or adsorbed water. Moreover, in addition to regular, cylindrical micropores, their structure exhibits irregular pores of larger diameters.

References

- [1] L. Bruce Railsback “*Some Fundamentals of Mineralogy and Geochemistry*”: www.gly.uga.edu/railsback/FundamentalsIndex.html
- [2] M. Kosmulski “*Surface charging and points of zero charge*”, Surfactant science series, vol. 145, CRC Press/Taylor & Francis Group, 2009.
- [3] M. Kosmulski, *Journal of Colloid and Interface Science*, 298 (2006) 730–741.
- [4] M.A.F. Pyman, J.W. Bowden and A.M. Posner, *Clay Minerals*, 14 (1979) 87-92.
- [5] J. Ościk, “Adsorption”, Ellis Horwood Limited, Publishers – Chichester, 1979.

Experimental

A. Equipment and reagents

1. Instrumentation:
 - Multifunction meter CX-401 ELMETRON;
2. Equipment:
 - 3 polypropylene vessels (60 mL);
 - Glass pipette (0.1 ml);
 - Measuring cylinder (50 ml).
3. Reagents:
 - Electrolyte: 0.1 M NaCl water solution (with the addition of HCl);
 - 0.1 M NaOH water solution;
 - Buffer solutions of pH equal to 4, 7 and 10;
 - Al₂O₃ (neutral);
 - SiO₂.

B. Task program

1. Calibration of pH-meter.
2. Preparation of oxide suspensions.
3. pH measurements during titration of oxides suspensions.

C. Specifying the task performance

Calibration of pH-meter

The multifunction meter CX-401 ELMETRON is shown in Fig. 9. Connect the pH electrode to seat 1 and temperature probe to seat 2. Switch on the pH-meter by pressing the button [FUNCTION]. Next press and hold the button [MODE] and after the symbol P.CAL appears on the display choose the symbol AUT using buttons with the arrows [↓] and [↑]. For calibration press the button [CAL].

In the bottom of display the symbol P1 will appear. Place the electrode and temperature probe into the first pH buffer solution (pH = 4). Make sure that the porous frit on the pH electrode is covered with your solution. If the pH meter does not screen correct pH value adjust it with the buttons with arrows. Press the button [CAL] to remember this value. After each measurement wash the electrode with distilled water and dab dry the bottom of the glass bulb of the electrode with a folded tissue paper. Do not wipe the glass bulb as it can produce interfering static charges or may permanently scratch the glass bulb affecting the electrode response. Next place the electrode and temperature probe into the second pH buffer solution (pH = 7). Adjust appropriate pH value and press [CAL] for memorization. Repeat this process once more for the third buffer (pH = 10). Ending the calibration press button [FUNCTION]. Now you can measure pH values of the investigated solutions.



Fig. 9. Multifunction meter CX-401 ELMETRON.

Measurements

Pour into each propylene vessel 50 mL of electrolyte solution (**E**). To one of them (**1S**) put 1 g of Al_2O_3 and to the other (**2S**) 0.7 g of Al_2O_3 and 0.3 g of SiO_2 .

Using the multifunction meter CX-401 ELMETRON measure pH values for electrolyte and both suspensions after adding subsequently 0.05 mL of 0.1 M NaOH solution and waiting for system equilibration during 20 minutes.

Collect the obtained data in Table:

V_{NaOH} [mL]	pH (E)	pH (1S)	pH (2S)
0			
0.05			
0.10			
0.15			
0.20			
0.25			

D. Analysis of results

In one figure draw plots $\text{pH} = f(V)$ for each investigated system.

Estimate the point of zero charge for Al_2O_3 and mixture of oxides.

Using equations (1) and (4) calculate surface charge of Al_2O_3 and SiO_2 in the mixture under PZC conditions. (Take into account converting the surface charge units from C/g into C/m^2 .) Take useful parameters from the specifications of nitrogen adsorption/desorption from Al_2O_3 and SiO_2 given on sites 14 and 15.

Micromeritics Instrument Corporation
 ASAP 2405N V ADSORBATE: NITROGEN
 SAMPLE DIRECTORY/NUMBER: DATA14 /233 START 10:08:02 03/24/09
 SAMPLE ID: **Al₂O₃** COMPL 18:32:57 03/24/09
 SUBMITTER: REPRT 08:08:46 03/25/09
 OPERATOR: SAMPLE WT: 0.8465 g
 STATION NUMBER: 1 EQUIL INTERVAL: 5 sec FREE SPACE: 93.4453 cc

SUMMARY REPORT

AREA

BET SURFACE AREA:	128.2239	sq. m/g
LANGMUIR SURFACE AREA:	162.4520	sq. m/g
SINGLE POINT SURFACE AREA AT P/P ₀ 0.1945:	125.7371	sq. m/g
BJH CUMULATIVE ADSORPTION SURFACE AREA OF PORES BETWEEN 17.0000 AND 3000.0000 A DIAMETER:	165.1519	sq. m/g
BJH CUMULATIVE DESORPTION SURFACE AREA OF PORES BETWEEN 17.0000 AND 3000.0000 A DIAMETER:	192.4010	sq. m/g
MICROPORE AREA:	1.3106	sq. m/g

VOLUME

SINGLE POINT TOTAL PORE VOLUME OF PORES LESS THAN 921.4639 A DIAMETER AT P/P ₀ 0.9785:	0.262623	cc/g
BJH CUMULATIVE ADSORPTION PORE VOLUME OF PORES BETWEEN 17.0000 AND 3000.0000 A DIAMETER:	0.271571	cc/g
BJH CUMULATIVE DESORPTION PORE VOLUME OF PORES BETWEEN 17.0000 AND 3000.0000 A DIAMETER:	0.265132	cc/g
MICROPORE VOLUME:	0.000675	cc/g

PORE SIZE

AVERAGE PORE DIAMETER (4V/A BY BET):	81.9263	A
BJH ADSORPTION AVERAGE PORE DIAMETER (4V/A):	65.7748	A
BJH DESORPTION AVERAGE PORE DIAMETER (4V/A):	55.1206	A

Micromeritics Instrument Corporation
ASAP 2405N V1.01 ADSORBATE: NITROGEN

SAMPLE DIRECTORY/NUMBER: DATA8 /178 START 12:23:03 07/07/06
SAMPLE ID: SiO₂ COMPL 04:40:01 07/08/06
SUBMITTER: REPRT 14:02:43 07/11/06
OPERATOR: SAMPLE WT: 0.3335 g
STATION NUMBER: 1 EQUIL INTERVAL: 10 sec FREE SPACE: 92.3843 cc

SUMMARY REPORT

AREA

BET SURFACE AREA:	313.8476	sq. m/g
LANGMUIR SURFACE AREA:	400.1624	sq. m/g
SINGLE POINT SURFACE AREA AT P/P ₀ 0.1964:	305.7672	sq. m/g
BJH CUMULATIVE ADSORPTION SURFACE AREA OF PORES BETWEEN 17.0000 AND 3000.0000 A DIAMETER:	350.2673	sq. m/g
BJH CUMULATIVE DESORPTION SURFACE AREA OF PORES BETWEEN 17.0000 AND 3000.0000 A DIAMETER:	415.8931	sq. m/g
MICROPORE AREA:	25.9297	sq. m/g

VOLUME

SINGLE POINT TOTAL PORE VOLUME OF PORES LESS THAN 2449.8213 A DIAMETER AT P/P ₀ 0.9921:	1.277959	cc/g
BJH CUMULATIVE ADSORPTION PORE VOLUME OF PORES BETWEEN 17.0000 AND 3000.0000 A DIAMETER:	1.286904	cc/g
BJH CUMULATIVE DESORPTION PORE VOLUME OF PORES BETWEEN 17.0000 AND 3000.0000 A DIAMETER:	1.278683	cc/g
MICROPORE VOLUME:	0.010409	cc/g

PORE SIZE

AVERAGE PORE DIAMETER (4V/A BY BET):	162.8763	A
BJH ADSORPTION AVERAGE PORE DIAMETER (4V/A):	146.9625	A
BJH DESORPTION AVERAGE PORE DIAMETER (4V/A):	122.9819	A