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**INFLUENCE OF INORGANIC CATIONS
ON ζ -POTENTIAL OF ALUMINA DISPERSIONS**

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The ζ -potentials of alumina dispersions were measured at two concentrations of monovalent electrolyte. Li^+ , Na^+ and K^+ were the investigated counterions, while the co-ion was always Cl^- . In comparison with the results of ζ -potential as a function of pH of pure Al_2O_3 without any added salts, the shift of isoelectric point (IEP) caused by added salts was observed. The values of IEP depend on the used counterion and on the concentration of the electrolyte which was added to dispersion of Al_2O_3 . The specific adsorption of cations shifts the IEP to higher values, while the specific adsorption of anions shifts the IEP to lower values.

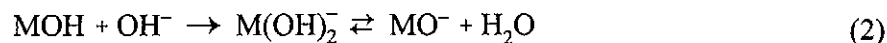
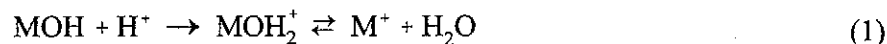
Introduction

Alumina is one of the most important materials as a membrane and also as a support. The charge of Al_2O_3 can be very useful for a filtration process where the alumina membranes are used.

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The surface charge of the alumina particles depends besides pH of the bulk solution on the kind of the added electrolyte and on the concentration of this electrolyte.

It is well known that if the surface of an oxide ceramic membrane is exposed to water, it becomes hydrated. The presence of water causes formation of the hydroxide layer containing MOH groups on the particle surface (M stands for a cation such Al^{3+} , Zr^{4+} , Si^{4+} or Ti^{4+}). These amphoteric MOH surface groups are enabled to dissociate when the surface gets in a contact with polar liquids. There are two mechanisms by which the surface charge of oxide materials can be achieved. These two mechanisms, the dissociation of surface groups and the adsorption of ions from the solution, often occur simultaneously. The dissociation of amphoteric surface groups strongly depends on the pH of the solution. The following two equations can express it



While the first reaction causes a positive charge (positive ζ -potential), the second produces a negative charge (negative ζ -potential) on the solid surface [1].

It means that the increasing pH from acidic to basic values causes a change in sign and magnitude of the alumina particle ζ -potential from positive to negative values. The pH value where the ζ -potential of particles is zero is called isoelectric point (IEP) [2].

Many studies [2–5] showed that the charge of alumina consists of two parts. One part is the alumina particle charge due to the dissociation of the ionisable groups of particle, and the other part is the alumina particle charge affected by the electrolytes in the bulk solution. This behaviour is typical of metal oxides, such as zirconia, rutile, anatase, silica, hematite, niobium and indium.

Greenwood and Kendall [6] studied the surface of alumina particles in the presence of KCl. They found that there exists a shift of the isoelectric point to higher values of pH when the concentration of KCl increases. This shift may be due to some adsorption of potassium ions at the alumina interface. The authors also found out that the values of ζ -potential were smaller in magnitude in the suspensions where the salt was present. This is due to screening of the surface charge by the electrolyte. The same results were shown by Gustafson and Macula [5]. They studied the influence of pH and NaCl on the ζ -potential of anatase

dispersions, and they also found that the isoelectric point is shifted to higher pH values with increasing salt concentrations. They also showed that addition of electrolyte affects the thickness of double layer and the magnitude of ζ -potential. The magnitude of ζ -potential will decrease with increasing concentration of added electrolyte.

Kosmulski, Gustafson and Rosenholm [7] investigated the rutile dispersion and its ζ -potential in the presence of Na^+ , Ca^{2+} , Ba^{2+} . Their results showed the existence of critical concentration of added electrolyte. When this concentration is exceeded there is no IEP and the ζ -potential is always positive. For example for anatase the IEP was found up to $\text{Ba}(\text{NO}_3)_2$ concentrations of $3 \times 10^{-3} \text{ mol dm}^{-3}$.

In his work, Franks [8] investigated the influence of Li^+ , Na^+ , K^+ and Cs^+ on the surface properties of silica particles. Hofmeister series (Cs^+ , K^+ , Na^+ , Li^+) order ions from the least to the most hydrated ions. He found that the adsorption sequence on the silica surface follows the Hofmeister series ($\text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$) with Cs^+ adsorbing in greater quantities than Li^+ . The measurements of ζ -potential indicate that addition of these ions affects the magnitude of the ζ -potential. The results obtained show that Cs^+ produces a lower magnitude than Li^+ . The results also showed that there exists a shift in the IEP to higher pH values as the salt concentration increases. This indicates that the alkali cations are adsorbing to the silica surface in quantities greater than required for charge neutralisation. The greatest shift in the IEP is found to follow the sequence from greatest IEP shift to least IEP shift $\text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$.

Kosmulski [9] studied the electrochemical properties of alumina in the presence of high concentration of certain 1-1 electrolytes. His results showed that the shift in the IEP induced by different salts comply with the following rules: Salts with large cations (Cs) have a rather insignificant and anion-independent effect. Salts with small cations (Li, Na) have a significant and anion-dependent effect. Salts with small anions (Cl) have a rather insignificant and cation-dependent effect.

The aim of the present work is to measure the ζ -potential of the alumina particles in the presence of LiCl, KCl and NaCl for two concentrations (0.001M to 0.005M) in the range of pH from 2 to 12. Next aim is to study the shift of the IEP and the magnitude of ζ -potential influenced by the kind and concentration of added electrolyte from the measured results.

Experimental

The alumina was of 99.9 % purity. The powder was further purified by repeated washing in solution of the ions and their concentration we wanted to work with.

The ζ -potentials of the alumina were measured at 0.001 and 0.005 M concentrations for each of LiCl, NaCl and KCl. The pH of measured solutions was

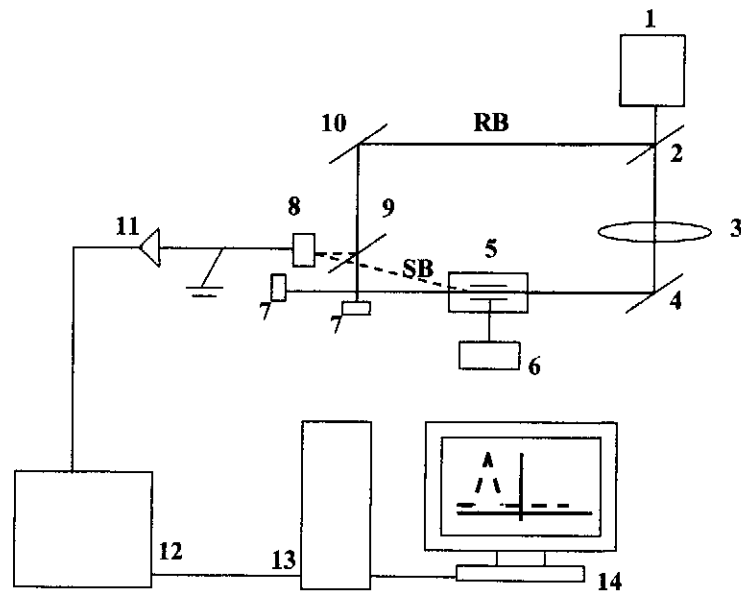


Fig. 1 Scheme of Zeta PALS Instruments: 1 – laser diode; 2 – beam splitter; 3 – lens; 4 – mirror; 5 – sample cell holder; 6 – generator of the electric field; 7 – light trap; 8 – detector; 9 – beam combiner; 10 – modulator; 11 – analyser of the spectrum or autocorrelator; 12 – digital adjustment into the average signal; 13 – output on PC; 14 – monitor; RB – reference beam; SB – scattered beam

changed by adding HCl or NaOH. All the chemicals used were of analytical grade and the solutions were prepared by using water from Reverse osmosis modul (Demiva 5 RO, WATER sr.o. Leděč nad Sázavou, Czech Republic), whose conductivity was less than $10 \mu\text{S cm}^{-1}$.

After changing the value of pH, the prepared samples were stirred on a magnetic blender for one hour. The samples were allowed to equilibrate for two hours before the ζ -potential measurement was performed.

The ζ -potentials of alumina particles were determined using a Zeta PALS instrument (Brookhaven Instruments Corp., USA – Fig. 1). The principle of measurement consists in the migration of charged particles under the influence of an electric field. The ζ -potential can be derived from the electrophoretic mobility

$$\zeta = \frac{\mu_M \eta}{\epsilon_0 \epsilon_r} \quad (3)$$

In Eq. (3), μ is the electrophoretic mobility, ζ is the ζ -potential, η is the dynamic viscosity of liquid, ϵ_0 is the permittivity of vacuum and ϵ_r is the relative

permittivity of the liquid. All the experiments were carried out at 25 °C.

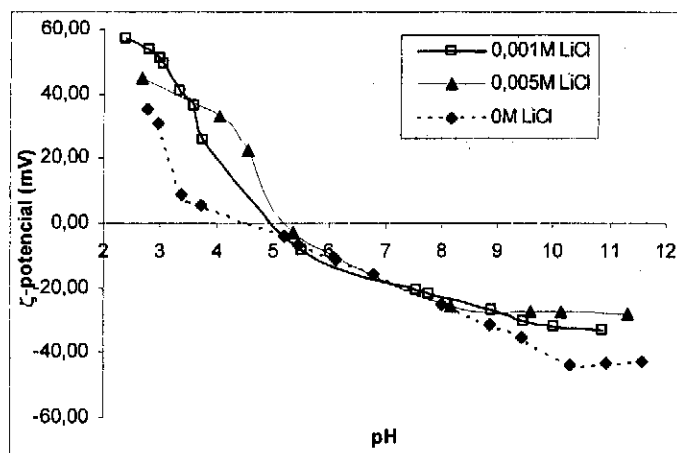


Fig. 2 The ζ -potential of alumina as a function of pH at various concentrations of LiCl

Results and Discussion

The isoelectric point (which is the pH at which particles have a ζ -potential zero) of alumina in demineralised water is 4.70.

The pH dependence of ζ -potential of alumina in LiCl solution at the two ionic strengths of 0,001 and 0,005 M is shown in Fig. 2. Besides these two curves in Fig. 2, there is also shown the pH dependence of ζ -potential of alumina in demineralised water (curve 0M LiCl). This dependence has an unexpected shape: the ζ -potential is negative at higher pH and becomes positive towards the lower end of the pH range. This behaviour may be explained by the proton equilibrium that occurs on the surface of alumina particles.

The same shapes of the pH dependences of ζ -potential of alumina are found in LiCl solutions. The IEP shifts to higher pH as the LiCl concentration increases. But we did not find such big differences. The IEP shifts from 4.70 (demineralised water without any salt) to 4.95 or 5.25 (value of IEP for alumina in 0.001 M LiCl or 0.005 M LiCl, respectively). The average magnitude of the ζ -potential in the area of negative ζ -potentials is greater in 0M LiCl than in 0.001M LiCl and in 0.001M LiCl than in 0.005 M LiCl; it means that the ζ -potential decreases with increasing ionic strength. These results may be explained by a decrease in the effective thickness of the diffuse layer as the ionic strength increases.

In the area of positive ζ -potential we expected the same behaviour as in the area of negative ζ -potential — i.e. the decrease in the magnitude of ζ -potential with increasing concentration of added electrolyte. This is probably because the

instrument software is unable to interpret the signal from large particles properly (the effective diameter of alumina at pH 5.48 was 4505.2 nm and it is well known that in the acidic area of pH the particles tend to aggregate, so that the size will be much bigger than 4500 nm [10]).

Figures 3 and 4 present the results obtained for NaCl, and KCl solutions, respectively. The results of ζ -potential of alumina in the presence of both electrolytes induce the shift in the IEP to higher pH, confirming the trend observed for LiCl.

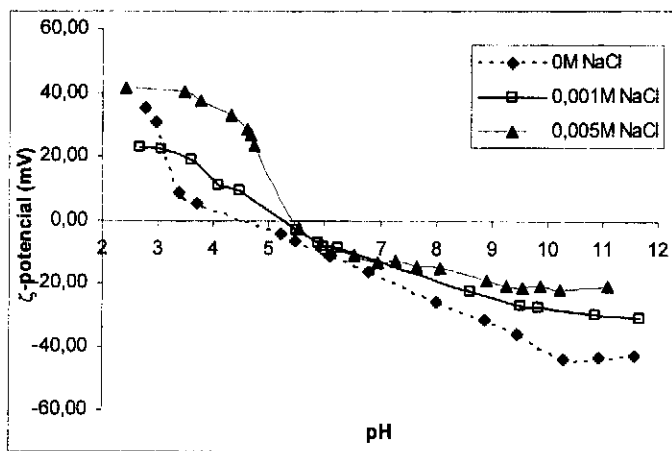


Fig. 3 The ζ - potential of alumina as a function of pH at various concentrations of NaCl

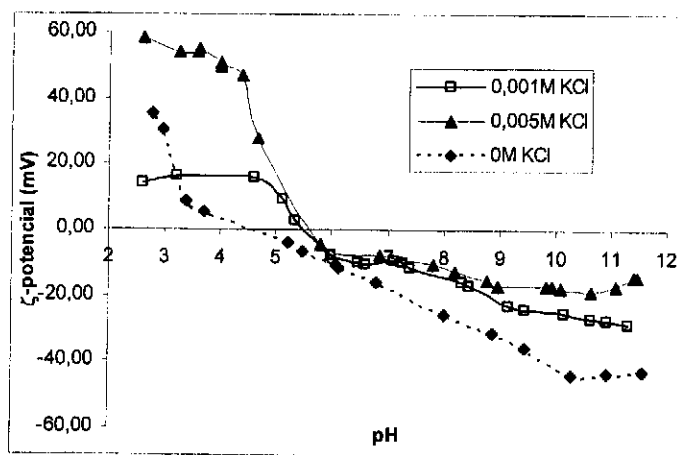
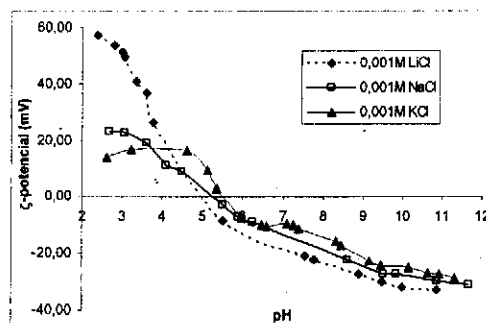
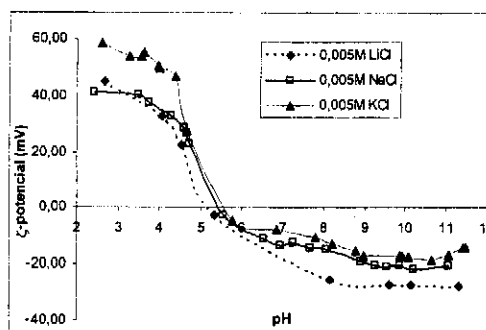


Fig. 4 The ζ - potential of alumina as a function of pH at various concentrations of KCl



(a)



(b)

Fig. 5 The ζ -potential of alumina as a function of pH, kind of electrolyte and concentration of electrolyte: a) 0.001M, b) 0.005M.

Figure 5 represents the ζ -potential values of alumina as a function of pH and kind of electrolyte for electrolyte concentrations a) 0.001 M and b) 0.005 M. The results indicate that the monovalent alkali cations specially adsorb and shift the IEP of alumina particles to higher pH values. It means that the alkali cations are adsorbing at the alumina surface in quantities greater than required for charge neutralization. For both concentrations of added electrolyte, at pH above the IEP, the magnitude of ζ -potential was found in the order $K^+ < Na^+ < Li^+$ consistent with the results of other investigators [8]. For both concentrations of added electrolyte we also found that the greatest shift in IEP follows the sequence from greatest IEP shift to the least IEP shift $K^+ > Na^+ > Li^+$.

The differences in the shift in IEP and in the magnitude of ζ -potential are caused by hydration of the used cations. The poorly hydrated ions (K^+) adsorb in greater quantity at the alumina surface than the well-hydrated ions (Li^+ and Na^+) and produce a lower magnitude of negative ζ -potentials at high pH. The shift in the IEP is also directly related to the hydration of the counterion with the least hydrated ions creating the greatest IEP shift.

Conclusion

The experimental data discussed in this paper show the values of ζ -potential as a function of pH, kind of added electrolyte and its concentration.

The results show that in alumina suspensions with increasing electrolyte concentration, the pH of the IEP shifts toward higher values. We obtained these results with all the electrolytes investigated.

The hydration of ion and diameter of the ion were found as parameters, which influenced the shift in the IEP and the magnitude of ζ -potential. The results indicate that the less hydrated ions (ions with bigger diameter) adsorb in greater quantities than well-hydrated ions (ions with small diameter) and shift the IEP to higher pH values and also produce less negative ζ -potentials at high pH.

Symbols

| | |
|-----------------|--|
| ε_0 | permittivity of vacuum, $F\ m^{-1}$ |
| ε_r | relative permittivity of the liquid |
| η | dynamic viscosity, Pa s |
| μ | electroforetic mobility, $m^2\ V^{-1}\ s^{-1}$ |
| ζ | zeta potential, V |

References

- [1] Moritz T., Benfer S., Árki P., Tomandl G.: *Sep. Pur. Tech.* **25**, 501 (2001).
- [2] Takagi R., Nakagaki M.: *Sep. Pur. Tech.* **25**, 369 (2001).
- [3] Nazzal F.F., Wiesner M.R.: *J. Membr. Sci.* **93**, 91 (1994).
- [4] Mullet M., Fievet J.C., Reggiani J.C., Pagetti J.: *J. Membr. Sci.* **123**, 255 (1997).
- [5] Gustafsson J., Mikkola P., Jokinen M., Rosenholm J.B.: *Colloids and Surfaces A.* **175**, 349 (2000).
- [6] Greenwood R., Kendall K.: *Powd. Tech.* **113**, 148 (2000).
- [7] Kosmulski M., Gustafsson J., Rosenholm J.B.: *Colloid Polym. Sci. Chem.* **277**, 550 (1999).
- [8] Franks G.V.: *J. Colloid Interface Sci.* **249**, 44 (2002).
- [9] Kosmulski M.: *Langmuir* **18**, 785 (2002).
- [10] Šmídová D., Mikulášek P., Mikulášek M.: *The influence of NaCl on microfiltration of anatase*, 31st International Conference of SSCHE, Tatranske Matliare, Slovakia, 2004.