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Stability of zirconia sol in the presence of various inorganic electrolytes

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Abstract: The zirconia sol was prepared from a zirconium oxychloride solution by forced hydrolysis at 102 °C. The prepared sol consisted of almost spherical, monoclinic, hydrated zirconia particles of 61 nm in diameter. The stability of zirconia sol in the presence of various inorganic electrolytes (LiCl, NaCl, KCl, CsCl, KBr, KI, KNO_3 and K_2SO_4) was studied by the potentiometric titration method. The dependence of the critical concentration of coagulation (*ccc*) on the dispersion pH was determined for all studied electrolytes. The critical coagulation concentration values for all investigated electrolytes were lower at higher pH values. These values for all 1:1 electrolytes were the same within the range of experimental error. For a given pH value, the *ccc*s of K_2SO_4 are 3–4 orders of magnitude lower than the corresponding values for the 1:1 electrolytes.

Keywords: zirconia sol; stability; electrolytes; critical coagulation concentration; potentiometric titration.

INTRODUCTION

For further development of nanostructured materials, new technologies that yield physically and chemically stable nanoparticles are required. Zirconia (ZrO_2) is an important ceramic material with an increasing range of applications, *e.g.*, for thin-film coatings and catalysis. An understanding of the surface charge characteristics as a function of pH and ionic strength is important in optimizing the processing conditions for high technology ceramics applications.[1] A colloidal dispersion is said to be stable when there is no significant agglomeration, *i.e.*, when the potential barrier is sufficiently high to prevent particles from contacting one another. Whether or not a dispersion is stable depends on both the surface

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electrostatic potential (dependent on dispersion pH) of the solid particles and the ion concentration in the solution.[2]

Coagulation of a colloidal dispersion may be affected by numerous factors, such as dispersion aging, change in the amount of the dispersion phase, mechanical and light action, change in temperature, *etc*. However, the coagulation caused by the addition of an electrolyte into a sol is of the greatest theoretical and practical importance. The interaction between a colloid and an electrolyte depends on the nature of the solid phase, especially on its surface composition, as well as on the type and concentration of ion species in the solution.[2] A fair amount of interest has also been shown in the stability of colloidal dispersions.[3–10]

Charged colloidal particles lead to the formation of a layer of opposite charge in the fluid adjacent to a particle – the so-called diffuse electrical double layer – that partly screens the charge on the particle. At low ionic strengths, the double layer extends beyond the range of the van der Waals force. The resulting electrical repulsion between the particles prevents agglomeration, unless the particles are nearly electrically neutral (which depends on the pH). At high ionic strengths, the double layer shrinks in size and the net force is always attractive. Hence, at high ionic strengths, agglomeration always occurs.

Surface charge at the metal oxide–electrolyte interface is formed by protonation or deprotonation of surface hydroxyl groups as well as the formation of other surface species from the background electrolyte ions (ion pairs or surface complexes). The structure of the inner region of the electrical double layer (edl) for such systems is very often described by the site-binding model.[11]

Most colloidal particles are electrically charged, *e.g.*, most metal oxides have surface layers formed by/made of hydroxyl groups which are amphoteric and can become either positively or negatively charged, by proton association or proton dissociation, depending on the pH:[12]

$$\geq Zr–OH + H^+ \rightarrow \geq ZrOH_2^+,\ pH < pH_{pzc} \quad (1)$$

$$\geq Zr–OH + OH^- \rightarrow \geq Zr–O^- + H_2O,\ pH > pH_{pzc} \quad (2)$$

Reaction (1) is favored by a low pH, while reaction (2) occurs at a high pH. pH_{pzc} represents the pH value at which the solid surface charge is equal to zero. For oxide systems, and many other colloids, H^+ and OH^- ions are the potential-determining ions. In such systems, the surface charge and potential are determined largely by the balance between H^+ and OH^- in the solution, *i.e.*, by the pH.

This paper presents a continuation of studies devoted to the study of inorganic sol stability. To the best of our knowledge, there are no literature data on the stability of colloidal zirconia in the presence of inorganic electrolytes; such a study is thus the aim of the present work.

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EXPERIMENTAL

The corresponding author's group has been successful in synthesizing different stable and monodisperse metal oxide sols using the forced hydrolysis method.

Zirconia sol was prepared from aqueous solution by the forced hydrolysis method, according to the procedure described in a previous paper,[13] using zirconium oxychloride octahydrate (Merck, *p.a.* grade) as the precursor and hydrochloric acid (35 % HCl, Lachema, *p.a.* grade). Doubly distilled water was used to prepare the acid solution. A solution of 0.01 M HCl was stirred in a reactor up to the boiling point (102 °C). The required amount of premixed $ZrOCl_2$ in 0.01M HCl solution was added to this solution under vigorous stirring and kept boiling under reflux for 24 h. This procedure was followed in order to avoid the local precipitation effect. The important parameters in direct synthesis are the choice of the type and concentration of precursors, solution pH, temperature and mixing.

In order to increase the stability of the prepared zirconia sol, it was ultrafiltered using an Amicon YCO5 membrane and an Amicon ultrafiltration cell (model 8200), until the permeate was free of chloride ions (negative $AgNO_3$ test). The ultrafiltered zirconia sol was stable (no precipitation) over 6 years. The zirconia particle size distribution was determined by the DLS (Dynamic Light Scattering) method using a Zetasizer Nano ZS with a 633 nm He–Ne laser (Malvern, UK). The Zetasizer Nano system is the latest generation of light scattering instruments, containing both the hardware and the software for combined static, dynamic, and electrophoretic light scattering measurements. A wide range of sample properties available for measurement with the system includes particle size, molecular weight and zeta potential. The instrument can measure particle sizes from 0.6 nm to 6 μm.

The stability of colloidal systems can be determined in various ways. One of them is the use of a classical and rather qualitative method consisting of a series of test tubes containing solutions with equal amounts of dispersed material, but with gradually increasing electrolyte concentrations. After a certain period, usually several hours, the point at which electrolyte concentration sedimentation or creaming had just occurred is visually established.[8,9,14,15] These experiments give better results than turbidity measurements.[14,15]

The coagulation of the zirconia sol containing different concentrations of electrolytes was monitored/examined. Eight different inorganic salts (LiCl, NaCl, KCl, CsCl, KBr, KI, KNO_3 and K_2SO_4) were used as electrolytes. These cations and anions were chosen with the aim of studying the relationship between the diameter size and the valence of ions and the pH of coagulation.

The employed experimental technique was potentiometric titration of separate samples.[2,4,5,16-18] PVC vessels containing the samples were equilibrated (with intensive mechanical stirring) for 4 h at room temperature. Then, each sample was visually examined; coagulation and phase separation, whenever it occurred, was noted.

RESULTS AND DISCUSSION

The particle size distribution of the zirconia sol, registered as the intensity during several successive DLS runs, is shown in Fig. 1. The experimental data are the average of at least six runs. Each curve/run presents a mean value of 14 measurements. The obtained average particle diameter represents the hydrodynamic diameter of a sphere (*i.e.*, diameter of a particle with a hydration shell), having the same volume as the particle. It is evident that the size distribution is monomodal and monodisperse. The polydispersity index (*PDI*) was 0.071, and

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the average zirconia particle diameter, d_{av}, 61 nm. As shown earlier,[13] the apparent crystallite size of the zirconia powder, calculated from XRD patterns according to the Scherrer equation, was about 6 nm. This means that zirconia particles in the prepared sol consist of several (up to ten) crystallites.

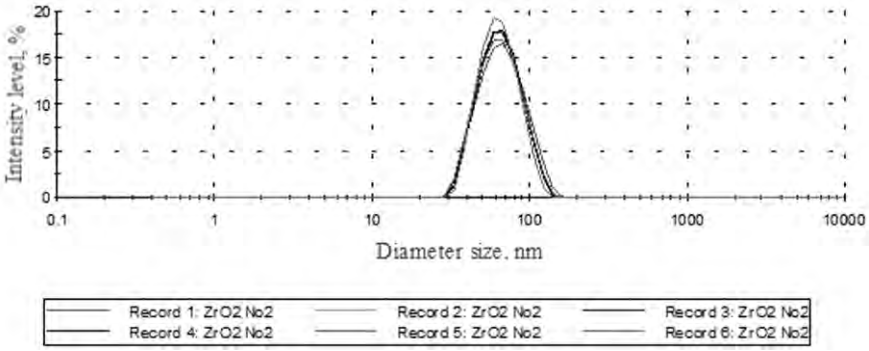

Fig. 1. Particle size distribution of the zirconia sol.

Before performing the coagulation measurements in the presence of selected inorganic cations and anions, the pH of coagulation (pH_c) of the zirconia colloid without electrolyte was found to be 7.75 (close to pH_{pzc} – point of zero charge of zirconia), by potentiometric titration with 0.1 mol dm^{-3} KOH. The stable, ultrafiltered zirconia dispersion (zirconia sol) used in this study had a pH value of 3.54.

Profiles of the logarithms of critical coagulation concentrations (log *ccc*, *ccc* is given in mol dm^{-3}) of the selected electrolytes (influence of anions and cations) as a function of pH_c show linear dependences (Figs. 2 and 3). The stability region for a given anion or cation is below and to the left side of the corresponding curve. For any point (pH_c, log *ccc*) chosen in this region, the stability of the system is preserved. On the other hand, the area above each curve and to its right side represents the coagulation region, *i.e.*, for any log *ccc* value at the corresponding pH_c, the coagulation is inevitable. For all the investigated electrolytes, the higher the critical coagulation concentration, the lower was the pH_c value.

For positively charged zirconia surface ($pH < pH_{pzc}$), near to pH_{pzc}, the critical coagulation concentration for monovalent anions increases in the following order: $NO_3^- \leq Cl^- < I^- \leq Br^-$. There is a slight difference in the pH_c values between the various monovalent anions at high salt concentrations.

The higher the $\Delta pH = pH_c - pH_{pzc}$ value, the more electrolyte is required to attain the critical coagulation concentration. Increasing ΔpH also causes an increase in surface charge of zirconia, which results in a more stable sol.

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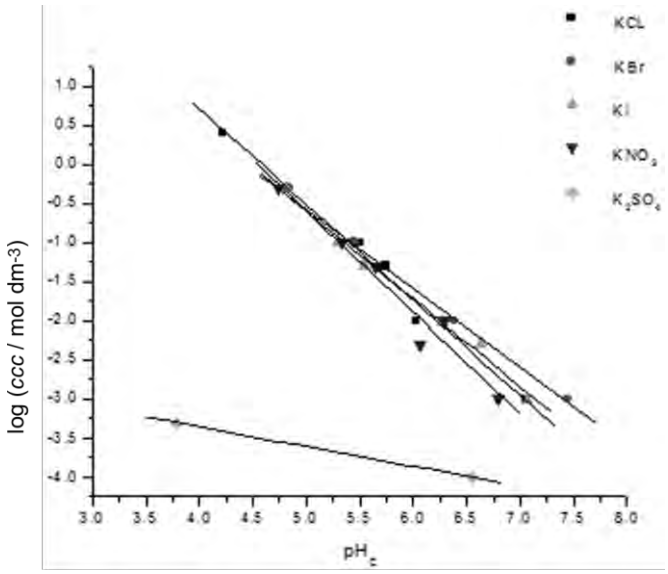

Fig. 2. Profiles of the logarithm of the critical concentrations of the selected anions as a function of pH_c.

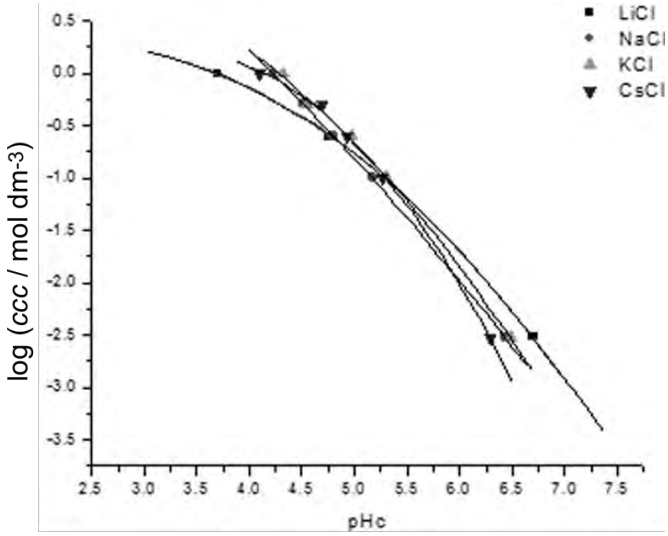

Fig. 3. Profiles of logarithm of the critical concentrations of the selected cations as a function of pH_c.

It can be seen from Fig. 2 that the critical coagulation concentrations of bivalent anion (SO_4^{2-}) for a given pH_c value were 3–4 orders of magnitude lower with respects to the corresponding values for monovalent anions.

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Pérez-Maqueda and Matijević[19] investigated the stability of a dispersion of zirconium (hydrous) oxide in the presence of $NaNO_3$, Na_2SO_4 and $H_4SiW_{12}O_{40}$. They obtained the following *ccc* values 3.5×10^{-3}, 7×10^{-5} and 2×10^{-4} mol dm^{-3} at pH 4 for NO_3^-, SO_4^{2-} and $SiW_{12}O_{40}^{4-}$, respectively. Comparing these values with the present results, it is evident that the herein studied sol was much more stable toward NO_3^-, SO_4^{2-} ions at this pH value. The following *ccc* values, at pH 4, for NO_3^- and SO_4^{2-} were 5.6 and 4×10^{-4} mol dm^{-3}, respectively (see Fig. 2). To obtain zirconium (hydrous) oxide particles, Pérez-Maqueda and Matijević[19] applied the precipitation procedure. They used solutions of zirconium chloride and triethanolamine (TEA). According to the XRD pattern, the zirconium hydrous oxide sample was amorphous. In addition, their procedure yielded stable dispersions at low temperatures and short reaction times.

A possible reason for SO_4^{2-} coagulation behavior lies in the specific character of the sulfate anion. The specific ion sorption changes the electrical properties of the electrical layer in different ways with respect to the simple attractive electrostatic interaction between non-specifically sorbed ions and the particle surface. For this reason, the Schultze–Hardy rule cannot be fully obeyed by the specifically sorbed anions. Besides, the critical coagulation concentration values for multi-charged ions are characteristic of a given system and cannot be generalized.

The minimum electrolyte concentration required to cause coagulation, known as the critical concentration of coagulation, for a divalent ion should be two-time lower than that for a monovalent ion, and for a trivalent ion, three times lower than that for a monovalent ion. This is the basis of the Schultze–Hardy rule: cZ^6 = constant, where c is the concentration of electrolyte and Z is the ion charge. The Schultze–Hardy rule is an empirical rule, stating that coagulation concentration of hydrophobic sols decreases very strongly with increasing valency Z of the counter-ion.[20]

For monovalent and divalent ions, the critical concentration of coagulation according to the Schultze–Hardy rule exhibited the proportion 1:0.016. The monovalent/divalent (SO_4^{2-}) anion ratio varied in the experiments from 0.0002 to 0.0129 for pH from 4.5 to 6.5. In practice, there was often evidence of deviations from this rule, mainly due to specific ion adsorption. Multivalent ions tend to adsorb on solid particles by specific binding. The interpretation of the Schultze–Hardy rule implies that the coagulation concentration is determined by a combination of specific ion adsorption and diffuse double layer overlap. The higher the ion valency, the higher is the contribution of the specific adsorption.[20]

CONCLUSIONS

Measurement of the particle size distribution proved the zirconia sol to be monomodal and monodisperse (with a polydispersity index 0.071). The obtained

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average zirconia particle diameter was 61 nm. Particles of initial zirconia sol were positively charged. The ultrafiltered zirconia sol was stable (no precipitation) for over 6 years. Eight inorganic electrolytes (LiCl, NaCl, KCl, CsCl, KBr, KI, KNO_3 and K_2SO_4) were added to the zirconia sol and potentiometric titration was performed in order to determine the stability of the sol in the presence of these cations and anions. The coagulation pH (pH_c), determined by potentiometric titration, varied from 4 to 7.5. The 1:1 electrolytes for cations of the same periodic group showed similar behavior. K_2SO_4 behaved differently showing much lower *ccc* values (3–4 times lower than for the 1:1 electrolytes).

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ИЗВОД

СТАБИЛНОСТ СОЛА ЦИРКОНИЈУМ(IV)-ОКСИДА У ПРИСУСТВУ РАЗЛИЧИТИХ НЕОРГАНСКИХ ЕЛЕКТРОЛИТА

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Извршена је синтеза мономодалног и монодисперзног цирконијум(IV)-оксида. Индекс полидисперзности добијеног сола је 0,071 а средњи пречник честица износи 61 nm. Честице припремљеног сола су позитивно наелектрисане. Полазни сол је стабилан у дужем временском периоду (дуже од шест година). Одређивана је стабилност синтетизованог сола у присуству осам одабраних неорганских електролита (LiCl, NaCl, KCl, CsCl, KBr, KI, KNO_3 и K_2SO_4). Вредности pH коагулације, у присуству наведених електролита, варирају у опсегу од 4 до 7,5. Електролити са једновалентним јонима имају слично понашање. Вредности критичних концентрација коагулације добијеног сола у присуству калијум-сулфата су 3–4 пута ниже у односу на оне за 1:1 електролите.

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REFERENCES

1. R. J. Xie, M. Mitomo, K. Uheda, F. F. Xu, Y. Akimune, *J. Am. Ceram. Soc*. **85** (2002) 1127
2. S. K. Milonjić, N. B. Vučić, *Mater. Sci. Forum* **282–283** (1998) 189
3. E. J. W. Verwey, J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids*, Elsevier, Amsterdam, 1948.
4. S. K. Milonjić, *Colloids Surf.* **63** (1992) 113
5. M. Petković, S. K. Milonjić, V. Dondur, *Bull. Chem. Soc. Jpn*. **68** (1995) 2133
6. J. D. F. Ramsay, S. R. Daish, *Discuss. Faraday Soc*. **66** (1978) 65
7. L. H. Allen, E. Matijević, *J. Colloid Interface Sci*. **33** (1970) 420
8. D. R. Harding, *J. Colloid Interface Sci*. **35** (1971) 172
9. M. Tschapek, R. M. Tores Sanchez, *J. Colloid Interface Sci*. **54** (1976) 460
10. R. Brace, E. Matijević, *Colloid Polym. Sci*. **255** (1977) 153
11. D. E. Yates, S. Levine, T. W. Healy, *J. Chem. Soc., Faraday Trans. 1* **70** (1974) 1807
12. J. Davis, R. O. James, J. O. Leckie, *J. Colloid Interface Sci*. **63** (1978) 480

Available online at shd.org.rs/JSCS/

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13. J. Marković, S. K. Milonjić, *J. Serb. Chem. Soc*. **71** (2006) 613
14. B. H. Bijsterbosch, *Stability of solid/ liquid dispersions,* in: *Solid/Liquid Dispersions*, Th. F. Tadros, Ed., Acad. Press, London, 1987, p. 91
15. E. Frey, G. Lagaly, *J. Colloid Interface Sci*. **70** (1979) 46
16. S. K. Milonjić, V. L. Razin, Yu. G. Frolov, *Kolloidn. Zh*. **42** (1980) 147
17. S. K. Milonjić, M. M Kopečni, Z. E. Ilić, *Bull. Soc. Chim. Beograd* **48** (1983) 351
18. A. Onjia, S. K. Milonjić, *Mater. Sci. Forum* **352** (2000) 111
19. L. A. Pérez-Maqueda, E. Matijević, *J. Mater. Res*. **12** (1997) 3286
20. J. Lyklema, *J. Colloid Interface Sci*. **392** (2013) 102.

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