Bull. Chem. Soc. Jpn., 68, 2133—2136(1995)

Stability of Colloidal Alumina in the Presence of Various Inorganic Anions

Milan Dj. Petković, Slobodan K. Milonjić,*,† and Vera T. Dondur

Faculty of Physical Chemistry, University of Belgrade, P.O. Box 137, 11001 Belgrade, Yugoslavia

†Chemical Dynamics Laboratory, Institute of Nuclear Sciences "Vinča",
P.O. Box 522, 11001 Belgrade, Yugoslavia

(Received July 29, 1994)

The stability of colloidal alumina in the presense of selected inorganic anions ($NO_3{}^-$, Cl^-, I^-, $SO_4{}^{2-}$, and $[Fe(CN)_6]^{3-}$) has been studied by a potentiometric titration technique. The dependencies of the critical concentrations of coagulation on the solution pH were determined for all studied anions, as well as the regions of coagulation and stability of the system. It has been shown that the critical concentrations of coagulation decrease along with an increase in the pH, which is interpreted by coagulation theory and the electrical layer model. Differences between the critical concentrations of coagulation at the same pH value for monovalent anions are explained based on their hydration degree differences, while the discrepancies between the experimental data and the theoretical values given by the Schultze–Hardy law are interpreted in light of specific sorption of sulfate anions and the general specificity of the investigated system. Based on a parallel stability study of colloidal alumina prepared in the laboratory and of a commercial product, the same stability behavior in the presence of KCl has been found.

Investigations of colloid systems containing an inorganic oxide as the solid and an aqueous electrolyte solution as the liquid phase have been of great interest during the past two decades. This fact can be closely associated with a growing list of different applications of the mentioned systems, together with similar applications of hydrous inorganic oxides in aqueous electrolyte solutions.

An especially intensive study was carried on various silica forms, amongst them colloidal silica, since it is a well-known industrial, material. However, a fair amount of interest has also been shown to hydrous alumina,[1—6] and to a much lesser degree to colloidal alumina.[7] The primary interest concerning these studies has been the adsorption of various adsorbates (ions, organic molecules and complexes) on an alumina surface. Although other studies have been dedicated to the preparation and aging conditions of colloidal alumina,[8] and the mechanisms of sol formation upon aging[9—11] or heterocoagulation,[12] very few have actually dealt with sol stability.[13]

To our knowledge there is no literature data on the stability of colloidal alumina in the presence of inorganic anions; such a study was thus the aim of the present work.

The surface properties and stability of a given colloid system belonging to the hydrophobic type can be successfully explained by the triple-layer electric-layer theory.[14—16]

The surface of a given inorganic oxide in an aqueous solution consists of amphoteric hydroxyl groups, which can be either protonated or deprotonated depending on the solution pH value, thus acquiring electrical charge.[15,16] In the case of a colloidal alumina particle, these processes can be represented as below:

$$\rangle AlOH + H^+ \rightleftharpoons \rangle AlOH_2^+ \quad (pH < pH_{pzc}); \tag{1}$$

$$\rangle AlOH + OH^- \rightleftharpoons \rangle AlOH^- + H_2O \quad (pH > pH_{pzc}). \tag{2}$$

Following the well-known and generally accepted Stern-Graham model,[17] which is a refined model of Gouy and Chapman (quoted in Ref. 17), a certain number of counter ions are accumulated near to the charged surface of a solid material, attracted by an electrostatic Coulomb attraction. They are likely to approach the surface at some distance (noted as β), which is close to the ionic radii of anions and the hydrated radii of cations. The ions closest to the surface are strongly bound to it, and form a so-called compact layer or a Stern layer of charge. It has been pointed out that the potential should decay linearly between the layer of surface charge (σ_0) and the compact layer charge (σ_β).[17] However, the surface charge is not entirely compensated by the compact layer charge of counter ions, and the remaining charge, necessary to make the system electro neutral, is distributed diffusely in the bulk liquid phase. The charge of this diffuse layer has been noted as σ_d, and the potential decay in this area should be exponential.

According to the generally accepted Gouy–Chapman–Stern–Graham model, charge and potential are assumed to be uniform in any particular layer, and the equation describing the distribution of charge is

$$\sigma_0 + \sigma_\beta + \sigma_d = 0. \tag{3}$$

The stability of a given colloid system strongly depends on the value of a property known as the electrokinetic or ζ-potential, which is equal to a difference between the compact layer potential and the diffuse potential. The greater is the ζ-potential, the more stable is the system because of a stronger Coulomb repulsion between the colloid particles, which prevents them from coagulating. It is evident that all extra counter ions added to the system tend to accumulate in the compact layer, thus decreasing the electrokinetical potential as well as the system stability regarding coagulation. The minimum electrolyte concentration required to cause coagulation, known as the critical concentration of coagulation (c_c) should be twice as small for a divalent ion than for a monovalent ion, and three-times as small for a trivalent ion with respect to the monovalent ion. This is the basis of the following Schultze–Hardy rule:[14)]

$$c_c \cdot z^6 = \text{const.} \tag{4}$$

For monovalent, divalent, and trivalent ions, the critical concentrations of coagulation should, according to the Schultze–Hardy rule, follow the proportion 729 : 11 : 1, respectively. However, these theoretical values are not respected in practice when one must take into account various factors such as specific adsorption, ion hydration, and specificity of a given system.

An important property of a colloid system is the point of zero charge (pzc), defined as the pH value at which $\sigma_0=0$, i.e. the number of positively charged surface centers (relatively small) equals that of negatively charged ones, so that the surface is electroneutral.[18)] This point should not be confused with the isoelectric one, defined as the pH value at which the ζ-potential equals zero. The two properties are identical only in the absence of specific ion adsorption.[18)]

Experimental

The colloidal alumina used in this study was prepared from an aluminium chloride solution by the hydrothermal peptization method in a similar way as to that described elsewhere.[8)] The obtained sol had a pH value of 3.12, which meant that the colloid particles were positively charged. The specific surface area of the solid phase, determined by a modified BET method,[19)] was found to be 203 $m^2\,g^{-1}$, and the solid phase content, determined gravimetrically, was 3.21 mass %.

The solid phase has a boehmite crystal structure, as shown by a Röntgen analysis on a Siemens Kristalloflex 4 with a Geiger–Müller counter. Colloid particles have a spherical form with a rather narrow size distribution, as ascertained by the transmission electronic-microscope method.

KNO_3, KCl, KI, K_2SO_4, and $K_3[Fe(CN)_6]$, obtained from various commercial sources, were of A.R. quality and used as received.

The experimental technique employed was potentiometric titration of separate samples. Each titration series consisted of samples, each having a volume of 50 cm^3 (solid content: 1 g AlO(OH) in 250 cm^3 solution). The concentrations of added electrolytes varied from 5×10^{-5} to 1.0 $mol\,dm^{-3}$; the pH (controlled by 0.1 $mol\,dm^{-3}$ KOH solution) ranged from (appr.) 4.0 to (appr.) 8.5, each sample having a pH value 0.5 higher than the precedent. The pH-meter (Beckman ϕ71) had a glass electrode and an electrolytical bridge containing a saturated calomel electrode immersed into exactly the same electrolyte solution as in the sample in order to eliminate any suspension efffect.[20)] The PVC vessels containing samples were equilibrated (with intensive mechanical stirring) for 4 h at room temperature. After that, each sample was visually examined; the coagulation and phase separation, whenever it occurred, was noted. The equilibrium pH values were measured, and the sample examination and pH measurements were repeated after 24 h.

The stability of a Kawaken Fine Chemicals Co., Ltd. commercial product in the presence of KCl and K_2SO_4 was studied in the same way as described above. This product, obtained by the hydrolysis of aluminium isopropoxide, also has a boehmite structure, but a greater specific area (472 $m^2\,g^{-1}$), and a fibrous from of particles.

Results and Discussion

Before performing stability investigations of colloidal alumina in the presence of selected inorganic anions (NO_3^-, Cl^-, I^-, SO_4^{2-}, and $[Fe(CN)_6]^{3-}$), a potentiometric titration of pure colloid alumina (without any electrolyte added) was carried out. It was found that the pH coagulation value for pure colloid is 6.58±0.37.

The dependencies of the logarithm of critical coagulation concentrations for all of the studied anions on the coagulation pH are presented Fig. 1. It can be seen that the coagulation pH decreases with an increase in the anion concentration in all cases, which is in accordance with the stability theory treating liophobic colloid systems and assuming the electrostatic repulsion forces between colloid particles to be of the same charge (positive in our case, since the peptization was carried out in acid medium). For significant monovalent anion concentrations (0.5—1.0 $mol\,dm^{-3}$) the system coagulates spontaneously without any addition of the base.

It can be observed that the critical concentrations of coagulation for all anions studied decrease with increasing pH. This is a logical consequence of the electrokinetic potential decrease of positively charged particles followed by an increase in the pH, a fact which influences negatively the system stability, so that lower electrolyte concentrations are needed for coagulation.

The stability region for a given anion is below its curve and on its left side. For any point (pH_c, $\log c_c$) chosen in this region the system stability is preserved. On the other hand, the area above each curve and on its

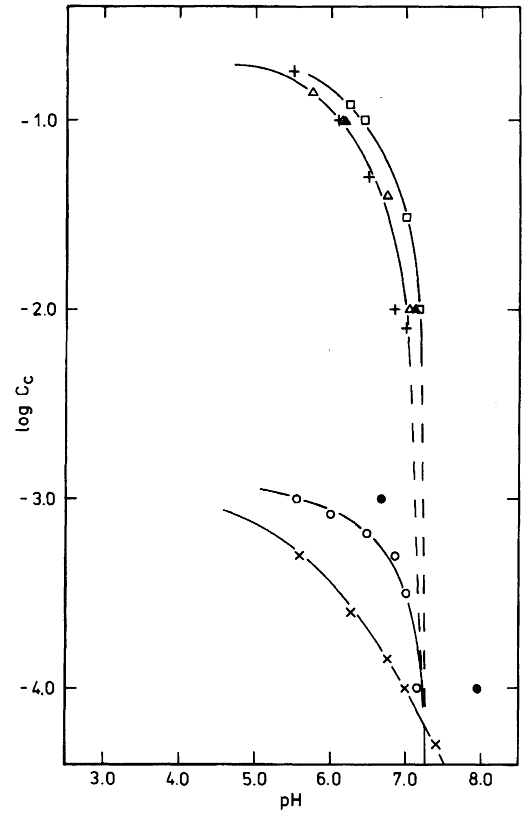

Fig. 1. Dependencies of log C_c on pH for laboratory prepared colloidal alumina at 22 °C for KNO_3 (+), KCl (△), KI (□), K_2SO_4 (○), and $K_3[Fe(CN)_6]$ (×). Full symbols (▲ and ●) belong to commercial (Kawaken) colloidal alumina for KCl and K_2SO_4, respectively.

right side represents the coagulation region, i.e. for any log c_c value at the corresponding pH_c the coagulation is inevitable.

Investigations of the Kawaken commercial product showed the same stability behavior in the presence of KCl as a sample prepared in the laboratory, while the stability behavior of two cited sols differed significantly in the presence of K_2SO_4 (see Fig. 1). The lower values of the coagulation pH for the commercial product of the same critical concentrations as in the case of the sol prepared in the laboratory suggest stronger surface binding of the sulfate ion. This is not a surprising fact, since it is well known that this particular anion can form complexes with hydrolyzed aluminium cations which can be situated on the surface;[11] and its adsorption thus acquires a specific character. The differences in the binding forces of the sulfate anion in the cases of two sols can be attributed to the different chemical characteristics of the solid-phase surfaces. These are the consequences of different sol preparation methods (hydrothermal peptization in our case and aluminium isopropoxide hydrolysis in the commercial product case).

It is interesting to note that all of the curves (except those for $[Fe(CN)_6]^{3-}$) cross the abscissa at one point, i.e., at pH=7.2 (Fig. 1). This value agrees reasonably with the point of zero charge (pH_{pzc}). However, the obtained higher value for $[Fe(CN)_6]^{3-}$ indicates its specific adsorption. It is also noteworthy that the specific adsorption of an anion shifts pH_{pzc} to higher pH values.[21]

Analyzing the data presented in Fig. 1, it can be concluded that no significant differences exist between the influences of monovalent anions on the stability of colloidal alumina. For positively charged boehmite surface ($pH < pH_{pzc}$), the critical coagulation concentrations for monovalent anions increase in the following order: $NO_3^- \leqslant Cl^- < I^-$. A greater coagulation power of the chloride anion with respect to iodide can be observed (Fig. 1). This is in accordance with the fact that the coagulation power of anions increases along with a decrease in their hydrations degree values.[22] Namely, a positively charged surface (represented by $>AlOH_2^+$ groups) interacts more intensively with a more hydrated anion because of a greater number of surface centers (compared with a neutral or negatively charged surface) available to attractive interactions with water molecules from hydrated anions, thus decreasing the electrokinetic potential. On the other hand, a negatively charged surface ($\rangle AlO^-$ groups) interacts more strongly with a less hydrated cation (i.e. with higher charge density). Since the chloride anion is more hydrated than the iodide one (the hydration enthalpy is -351.1 kJ mol^{-1} compared with -280.1 kJ mol^{-1} for iodide[23]), its critical concentration of coagulation is, consequently, lower. The lowest critical concentration of the coagulation exhibites NO_3^- for $pH \geqslant 6.25$, in spite of a hydration enthalpy value of -309.3 kJ mol^{-1} (Ref. 24), which lies between the cited values for Cl^- and I^-. This fact could be explained by a characteristic chemical structure (four electronegative atoms linked together) which offers a greater opportunity for a relatively strong electrostatic interaction with surface centers than in the case with mononuclear anions.

More drastic is the influence of multivalent anions on the sol stability. From Fig. 1 it can be seen that for a given pH value the critical coagulation concentrations of multivalent anions are lower for 2—3 orders of magnitude with respect to the corresponding values for monovalent anions. This is again in accordance with coagulation theory, since the charge required for rendering the electrokinetic potential to the critical value is constant for a given system.

The ratios of the critical coagulation concentrations of electrolytes studied at pH=6.50 are presented in Table 1. The data presented in Table 1 follow the theoretical ratio given by the Schultze–Hardy law only approximately. A possible reason for this coagulation behavior lies in the specific character of the sulfate anion, as mentioned above. The specific ion sorption changes the electrical properties of the triple electric layer in a different way with respect to the simple attractive electrostatic interaction between non-specifically sorbed ions and the

Table 1. Ratios of Critical Consentrations of Coagulation for the Electrolytes Studied at pH=6.50

$C_{\mathrm{KNO_3}} : C_{\mathrm{K_2SO_4}} : C_{\mathrm{K_3[Fe(CN)_6]}}$	250 : 3.3 : 1
$C_{\mathrm{KCl}} : C_{\mathrm{K_2SO_4}} : C_{\mathrm{K_3[Fe(CN)_6]}}$	315 : 3.3 : 1
$C_{\mathrm{KI}} : C_{\mathrm{K_2SO_4}} : C_{\mathrm{K_3[Fe(CN)_6]}}$	455 : 3.3 : 1

surface. For that reason, the Schultze–Hardy law cannot be fully obeyed by the spacifically sorbed anions. Besides, the ratio of the critical coagulation concentration values for multi-charged ions is characteristic for a given system, and cannot be generalized. It can be shown that the critical coagulation concentration ratio for two ions depends on several parameters,[22] such as the mean distance between a water molecule bound to a surface-active center and the counter ion, water dipole moment, ion charge, and value of the local dielectric constant in the triple-layer region, which differs greatly from the bulk-phase value, and could be even close to the value of 1 in some cases.[24] It can be concluded that in considerations like this one must also include the structure and properties of the triple electric layer, anion species, as well as the solvent properties.

The critical coagulation concentration ratio of KI, K_2SO_4, and $K_3[Fe(CN)_6]$ approaches most closely the theoretical values given by Schultze and Hardy in the 6.50—6.75 pH region. Since in this very narrow region is located the point of zero charge of colloidal alumina, the system stability is considerably decreased while at the same time its sensitivity to multivalent anion presence is increased.

The autors are indebted to Mr. Kiyoshi Niino (Kawaken Fine Chemicals Co., Ltd., Tokyo, Japan) for alumina sol sample gifted.

The work was partially supported by the Ministry of Sciences, Serbia.

References

1) C. P. Huang and W. Stumm, *J. Colloid Interface Sci.*, **43**, 409 (1973).

2) W. Smit and C. M. L. Holten, *J. Colloid Interface Sci.*, **78**, 1, (1980).

3) K. Hachiya, M. Sasaki, Y. Saruta, N. Mikami, and T. Yasunaga, *J. Phys. Chem.*, **88**, 23 (1984).

4) A. R. Bowers and C. P Huang, *J. Colloid Interface Sci.*, **105**, 197 (1984).

5) W. F. Bleam and B. McB. Murray, *J. Colloid Interface Sci.*, **103**, 124 (1985).

6) K. M. Philips and J. P. Wightman, *J. Colloid Interface Sci.*, **108**, 495 (1985).

7) L. Righetto, G. Bidoglio, B. Marcandelli, and I. R. Bellobono, *Radiochim. Acta*, **44/45**, 73 (1988).

8) E. V. Konakov, L. B. Prokhorova, and O. M. Merkutev, *Kolloid. Zh.*, **49**, 769 (1987).

9) T. Maki and S. Sakka, *Bull. Inst. Chem. Res. Kyoto Univ.*, **65**, 242 (1987).

10) R. Brace and E. Matijević, *J. Inorg. Nucl. Chem.*, **35**, 3691 (1973).

11) D. L. Catone and E. Matijević, *J. Colloid Interface Sci.*, **48**, 291 (1974).

12) T. W. Healy, G. R. Wiese, D. E. Yates, and B. V. Kavangh, *J. Colloid Interface Sci.*, **42**, 647 (1973).

13) J. D. F Ramsay and S. R. Daish, *Discuss. Faraday Soc.*, **65**, 65 (1978)

14) Yu. G. Frolov, "Kurs Kolloidnoi Khimii," Khimiya, Moskva. (1982).

15) J. A. Davis, R. O. James, and J. O. Leckie, *J. Colloid Interface Sci.*, **63**, 480 (1978).

16) R. O. James and G. A. Parks, in "Surface and Colloid Science," ed by E. Matijević, Plenum Publishing, New York (1982), pp. 119—216.

17) D. C. Graham, *Chem. Rev.*, **41**, 441 (1947).

18) N. Kallay, V. Hlady, J. Jednaček-Biščan, and S. Milonjić, in "Investigations of Surfaces and Interfaces," ed by B. W. Rossiter and R. C. Baetzold, Part A, Chap. 2, "Physical Methods of Chemistry," John Wiley & Sons, New York (1993), pp. 73—140.

19) *Pure Appl.Chem.*, **57**, 603 (1985).

20) G. H. Bolt, *J. Phys. Chem.*, **61**, 1166 (1957).

21) S. K. Milonjić, Ph. Thesis, University of Belgrade, Belgrade, 1981.

22) V. I Yashkichev and Yu. M. Dergachev, *Zh. Fiz. Khim.*, **66**, 1252 (1992).

23) N. A. Izmailov, "Elektrokhimiya Rastvorov," Khimiya, Moskva (1976).

24) O. Ya. Samoilov, *Zh. Strukt. Khim.*, **7**, 15 (1966).