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Ultrasonic vibration potential and point of zero charge of some rare earth oxides in water

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Abstract

The surface charge of rare earth metal oxides in water was examined using ultrasonic vibration potential (UVP) technique for the dilute colloid. Sonic irradiation induced an alternative current in suspensions of oxide powders in water. The observed potential largely varied, depending on the surface charge density of oxide powders, for suspensions at different pH as well as the kind of rare earth metals used. The paper described the measurement results and comparison for several rare earth oxides. The effect of pH and its swing and the kinds of rare earth element in oxides were reported. The point of zero charge (p.z.c., pH of zero charge for powders in water) strongly depended on the kinds of metal elements forming oxides and valence of metal ions. For a series of rare earth elements, dependence of atomic number can be observed; however, the distinguishing feature was the difference between trivalent rare earth metal oxides and tetravalent Ce oxide. The p.z.c. of CeO_2 was 6.7, while those of oxides of trivalent rare earth were 8.3–8.8.

Keywords: Ultrasonic vibration potential; Point of zero charge; Zeta potential; Rare earth oxide; Ce

1. Introduction

In the colloidal processing of metal oxide powders, it is important that the particles are well dispersed so that no aggregates form in water. Essentially the metal oxide particles should have repulsive force separating the particles from one another in their colloidal states. Depending on pH in water, the surface charge density varies because charged species including H^+ or OH^- adsorbed on the particles. Sonic irradiation induced an alternative current in suspensions of oxide powders in water [1]. The observed ultrasonic vibration potential (UVP) largely varied, depending on the surface charge density of powders or molecules, for suspensions at different pH as well as the kind of species used. The charge situation is in detail described by the electric double layer that forms at the oxide/solution interface in the colloid. Very little systematic study to understand the colloidal properties of rare earth oxides has been performed so far despite the increasing activity of rare earth metal oxides/water system in various fields such as catalyst and ceramics. This work describes the ultrasonic vibration potential behavior of several rare earth oxides in water, and then the zeta potential and the point of zero charge measured for them.

2. Experimental

2.1. Method

The ultrasonic vibration method measures the alternative electric potential, which is induced by alternative acoustic wave, applied to colloidal system [2]. In water containing particles, when as-charged particles are, and then the outer shell of counter ions lags behind by the sound wave, a dipole moment around particles is created. Using the electrodes set in corresponding wavelength, the electric potential, which is induced by ultrasonic vibration, can be measured. This is called ultrasonic vibration potential. UVP is related by zeta potential, if the density of particles, viscosity and density

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of liquid (water), electric conductivity of particle and liquid and volume fraction of particle are known. In this work, we used a UVP-measuring apparatus, an acoustophoretic titrator system 7000 designed by Pem Kem Inc. (Bedford hill, NY, USA). All parameters for the colloids are measured or controlled to calculate the UVP and the zeta potential. Typical sonic amplitude and frequency were 5×10^3 N/m^2 and at 250 kHz, respectively.

2.2. Samples and procedure

We used a series of reagent grade (99.9%) rare earth metal oxides (Y_2O_3, CeO_2, Nd_2O_3, Sm_2O_3, Dy_2O_3, Er_2O_3) purchased from Shin-etsu Chemistry Co. and α-Al_2O_3 (99.99%) received from Sumitomo Chemistry Ltd. for UVP measurement. The powder of 0.1 vol% in water was dispersed in ion-exchanged water. The UVP measurement is performed from acid side to base region during the titration of 1 M KOH solution in the range of pH 6–12 at the first time. Then, by adding 1 M HCl solution, the UVP was measured back in the region of pH 12–6.

3. Results and discussion

3.1. Ultrasonic vibration potential

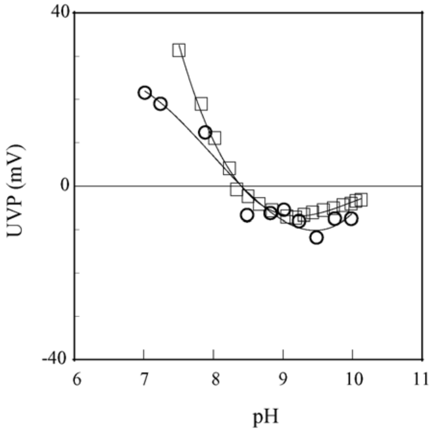

Fig. 1. Ultrasonic vibration potential of Sm_2O_3 (0.1 vol% in water) measured for a titration cycle (□, first; ○, second) in pH 7–12.

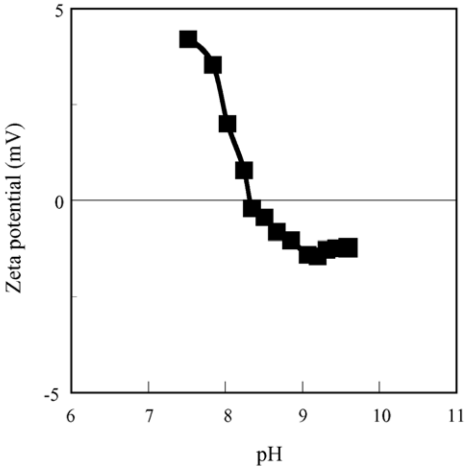

Fig. 2. Zeta potential of Sm_2O_3 calculated from UVP and conductivity for a colloid solution.

Fig. 1 shows the relationship between UVP and pH for Sm_2O_3 in water during a cyclic titration with KOH and HCl. First, the large UVP amplitude of 40 mV was observed for a colloidal system of Sm_2O_3 powder in pure water as prepared. By adding KOH solution, the UVP become to decrease, and then crossed over zero when pH 8.3 and changed to negative potential in high pH region. The phenomenon is essentially related to the surface charge density on dispersed particles, depending on the concentration of H^+ and OH^- in water. On the way back to lower pH, the amplitude of UVP was slightly lower than those in the first run. In the experiment about Sm_2O_3, the point of zero charge (p.z.c.), which was a cross-point on pH with zero UVP, was 8.3 ± 0.2. Since the addition of electrolytes (KOH and HCl) results in the increase of conductivity of solutions, the resultant voltage amplitude (UVP) picked up from a colloid must decrease due to the electronic discharge via a solution. So, we measured the conductivity during titration at the same time. The zeta potential (ζ) should be described by following equation [3]:

$$\mathrm{UVP} = \frac{2P}{\rho_0}\frac{\phi}{\lambda_0}(\rho_1 - \rho_0)\frac{\varepsilon_0\varepsilon_r\zeta}{\eta}$$

where P is the pressure of ultrasonics, ϕ the volume fraction of solid in colloid, ρ_1 the density of solid, ρ_0 the density of liquid, λ_0 the conductivity of solution, ε_0 the dielectric constant of vacuum, ε_r the specific dielectric constant of solution and η is the specific viscosity of solution. Fig. 2 shows the calculated the zeta potentials for Sm_2O_3 from UVP in the first run (corresponding to Fig. 1 using conductivity data). The data for a series of rare earth oxides show similar pH-dependent tendency for each UVP measurement. The zeta potential is defined by the potential at shearing interface (near surface) between particles and solution (in double layer) when the particle moves in solution. In the ideal condition, this should be determined by the situation of double layer near particle/solution interface, which is actually complex and affected by the concentration of electrolytes and surface charge of particles as well as pH. Thus, during the titration, the surface situation near particle surface and the precise distance from surface determine zeta potentials should vary by mixing K^+ and Cl^- and their concentrations. For this reason, the small inconsistency between the data of p.z.c. and zeta potential might be found for these and previous experiments every time when certain acid or base with different concentration is selected to control pH. To measure the p.z.c. of oxides, we determined that the value in the first run was more reasonable as p.z.c. in pure water.

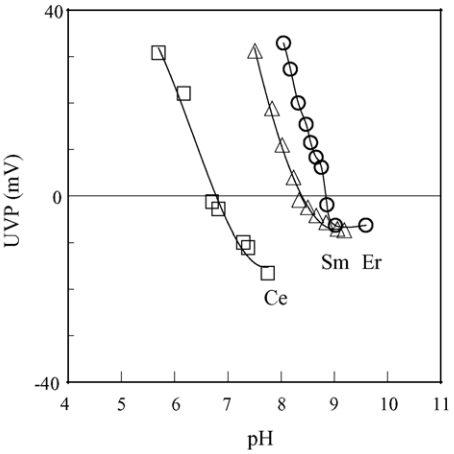

Fig. 3. The plots of UVP vs. pH for CeO_2 (□), Sm_2O_3 (△) and Er_2O_3 (○).

3.2. *Point of zero charge*

In Fig. 3, we estimate the difference in the relationship of UVP versus pH among three rare earth oxides, and find dependence upon valence of metal elements in oxides, CeO_2, Sm_2O_3 and Er_2O_3. From an aspect of catalysis, the p.z.c. should be low for acidic oxide and high for basic oxide. While several ionic species may be adsorbed for metal oxides, the p.z.c. refers to specific adsorption of OH^- and H^+. The p.z.c. is then pH at which the net surface charge is zero. If the appropriate hydroxylated or protonated species (surface structure) and their free energies of formation on surface are known, it is possible to determine precisely electronic potential (and the shift of pH) for the resultant species. However, this is difficult in general, because of complexity of surface structure and composition. From the plots of UVP versus pH, we measured the p.z.c. of metal oxides in water for a series of rare earth oxides. Table 1 summarizes the point of zero charge for a series of metal oxides. The value of Al_2O_3 as reference seemed to be consistent with those of the previous reports [4–8]. The measured data of p.z.c. for Al_2O_3 were 6.7 [4], 8.4 [5], 9.1 [6] and 9.4 [7], depending on the preparation of powder and colloid with electrolytes. Since Al_2O_3 shows both acidic and basic properties on the surface site, a procedure such as pre-heat treatment can affect on resultant p.z.c. Although little worker have measured the p.z.c. of rare earth oxides, the p.z.c. of CeO_2 is reported as 6.75 in an old reference by Mattson and Pugh [9]. Recently, Syrycha et al. [10] reported that the isoelectric point and p.z.c. of Y_2O_3 in aqueous $NaClO_4$ solution was 9.1 for a powder heated at 900 °C. Since the surface charge density refers to all species in solution, we must take care for the calculation of the zeta potential and the isoelectric point. Nevertheless, the p.z.c. of CeO_2 was consistent with that of a previous one. For the p.z.c. of Y_2O_3, difference of 0.8 in pH (8.3 in our work and 9.1 in ref. [9]) was found. Although the influence of electrolytes in water should be examined more for each colloid system using various ion species in water, at the least, all the p.z.c.s represent the criterion of positive or negative charge in water with dilute electrolytes for these rare earth oxides. Our measurement is the first systematic work on a series of rare earth oxides using the same method. We determined the p.z.c. of colloidal rare earth oxides under the condition of dilute electrolytes in water. In conclusion, the p.z.c.s were 8.3 (±0.2)–8.8 (±0.2) for trivalent rare earth oxides, while 6.7 for CeO_2, thus difference among elements could be critically found.

Table 1
Point of zero charge (p.z.c) for several rare earth oxides

Metal oxide	p.z.c. (pH)
Y_2O_3	8.3
CeO_2	6.7
Nd_2O_3	8.4
Sm_2O_3	8.3
Dy_2O_3	8.8
Er_2O_3	8.8
Al_2O_3	8.3

4. Summary

The effect of pH and its swing and the kinds of rare earth element in oxides on ultrasonic vibration potentials was examined. The point of zero charge of oxides in water depended on the kinds of metal elements forming oxides and valence of metal ions. For a series of rare earth elements, dependence of atomic number can be observed; however, the distinguish feature was the difference trivalent rare earth metal oxides and tetravalent Ce oxide. The zero charge point of CeO_2 was 6.7, while those of oxides of trivalent rare earth were 8.3–8.8.

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References

[1] A.J. Rutgers, J. Vidts, Nature 165 (1950) 109.
[2] E. Yeager, H. Dietrick, F. Hovork, J. Acoust. Soc. Am. 25 (1953) 456.
[3] R. Zona, E.B. Ernest, Mod. Aspects Electrochem. 14 (1982) 1.
[4] M. Robinson, J.A. Pask, D.W. Fuerstenau, J. Am. Ceram. Soc. 47 (1964) 516.
[5] P.G. Johansen, A.S. Buchanan, Aust. J. Chem. 10 (1957) 398.
[6] J.A. Yapps, D.W. Fuerstenau, J. Colloid Sci. 19 (1964) 61.
[7] H.S. Modi, D.W. Fuerstenau, J. Phys. Chem. 61 (1967) 640.
[8] G.A. Parks, Chem. Rev. 65 (1965) 177.
[9] S. Mattson, A.J. Pugh, Soil. Sci. 38 (1934) 229.
[10] R. Syrycha, J. Jablonski, E. Matijivic, J. Colloid. Interface Sci. 149 (1992) 561.