The Point of Zero Charge, Differential Capacity of the Electrical Double Layer & Interfacial Free Energy at Tin Dioxide-Aqueous Solution Interface

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Adsorption studies of potential-determining ions (H\(^+\) and OH\(^-\)) at the tin dioxide-aqueous solution interface as function of pH and ionic strengths in NaCl and NaNO\(_3\) solutions have been made in the pH range 3-8. The point of zero charge (PZC) of the tin dioxide precipitate has been determined by the intersection of fast adsorption isotherms. Isoelectric point determined by electrophoretic mobility measurements of suspended tin dioxide particles at different ionic strengths maintained by NaCl has been found to coincide with PZC of the oxide. Na\(^-\), Cl\(^-\) and NO\(_3\) are found to have no specific affinity for the uncharged tin dioxide-aqueous solution interface. The minimum values of the differential capacities of the electrical double layer have been evaluated from the fast adsorption isotherms in the presence of NaCl and NaNO\(_3\) by graphical differentiation of fast adsorption isotherms. These values not only agree well with each other within the limits of experimental error but also are very close to the value (6 \(\mu\)F/cm\(^2\)) obtained by Grahame on mercury-solution interface. The interfacial free energy change with respect to PZC has also been studied as function of surface charge density and ionic strengths.

In two previous publications\(^1\)\(^-\)\(^2\), we reported the results of our investigations on chromic oxide-solution interface and zirconium oxide-solution interface. Potentiometric acid-base titrations and electrophoretic mobility measurements were used for obtaining the quantitative information on the characteristics of the electrical double layer, such as pH dependence of surface charge, the point of zero charge (PZC), the differential capacity and the interfacial free energy.

Although by definition one PZC value characteristic of each oxide system would be expected, variations in the PZC of oxides depending on the experimental conditions and methods employed have been reported\(^3\)\(^-\)\(^4\). Concerted effort to account for the variation is limited. Block \textit{et al.}\(^3\)\(^-\)\(^4\) pointed out that pH variations resulting from the addition of acid or base to an oxide solution proceed in two steps with different time constants. According to them, the fast step describes the true response of the interface to the changes in composition of the solution phase (pH and ionic strength). The slower step is generally believed to arise out of the compositional changes involving the surface regions of the bulk solid phase. While accepting the above views, a detailed description of the oxide solution interface may be given in the following way.

When a sparingly soluble oxide is added to an electrolyte solution, the possible reactions which may occur are: (a) hydrolysis and complex formation of the surface atoms and subsequent dissociation of the surface groups; these reactions may be considered to be the primary step which is followed by (b) dissolution of the oxide material leading to secondary reactions which may consist of hydrolysis, complex formation and dissociation of the dissolved complexes of the surface and precipitation or colloid formation. Since the primary equilibrium of the surface (type-a) with the potential-determining ions (H\(^+\) and OH\(^-\)) involves charging of the electrical double layer at the interface, it should be complete within a few minutes after the addition of acid or base to the oxide suspension. The secondary reactions (type-b) are found to be very slow\(^5\)\(^-\)\(^8\). The secondary reactions (type-b) resulting in the slow variation in pH which generally follows the fast adsorption step (type-a) may be attributed alternatively to a kinetically slow ion-exchange process. For these two equilibrium conditions, PZC probably will be different. Since the primary oxide-solution equilibrium (fast, type-a) depends on the dissociation constants of the surface-OH groups in contact with the electrolyte solution, PZC and other parameters of the electrical double layer evaluated from the study of the surface under fast equilibrium condition may be considered to be more reliable than those obtained from slow equilibrium measurements.

In this paper, we report and discuss the results obtained in the study of the tin dioxide-aqueous solution interface which is concerned with the primary interactions of the surface with H\(^+\) and OH\(^-\). The secondary step of slow pH change which introduces complications and hence errors in the
evaluation of double layer characteristics has been reduced to minimum as far as practicable in the present investigation. The primary equilibrium of the surface with the potential determining ions (H⁺ and OH⁻) is found to be completed within 5 min of the addition of acid or base to the tin dioxide suspension whereas the secondary slow step lasts for 2-3 hr. By restricting the acid-base titrations of the tin dioxide suspension by the potentiometric method within 5 min of each addition of acid or base the fast adsorption isotherms have been constructed and PZC of the oxide has been determined from the intersection of these isotherms at various ionic strengths. Differential capacity of the electrical double layer and the interfacial free energy at tin dioxide-aqueous solution interface have been calculated on the basis of these fast adsorption isotherms. With a view to comparing PZC obtained by the fast adsorption measurement method with the pH of the zero mobility of the oxide particles, microelectrophoretic mobility measurements of the suspended tin dioxide particles have also been made at various ionic strengths.

Materials and Methods

The chemicals used were of AR grade. The tin dioxide suspension was prepared by precipitation from aqueous solutions of stannic chloride with ammonia. The precipitate was boiled under reflux for seven days, filtered, washed with conductivity water by centrifugation and decantation until free from chloride ions. The specific conductivity of the supernatant liquid was found to be less than that of 10⁻³M KCl solution at the same temperature. Tin dioxide was prepared in different batches using the same experimental procedure and stored in polythene bottles to avoid silicate contamination. The specific surface area of the oxide, as determined by BET method was 40.3 m²/g.

The adsorption isotherms of H⁺ and OH⁻ obtained by the acid-base potentiometric titration of SnO₂ suspension in the presence of supporting electrolyte NaCl are shown in Fig. 1. Concentrations used were 10⁻³, 10⁻², 5 × 10⁻² and 10⁻¹ and 5 × 10⁻¹M in each case. Similar adsorption isotherms have been found to be completed within 5 min of each addition of acid or base to the tin dioxide suspension whereas the secondary slow step lasts for 2-3 hr. By restricting the acid-base titrations of the tin dioxide suspension by the potentiometric method within 5 min of each addition of acid or base the fast adsorption isotherms have been constructed and PZC of the oxide has been determined from the intersection of these isotherms at various ionic strengths. Differential capacity of the electrical double layer and the interfacial free energy at tin dioxide-aqueous solution interface have been calculated on the basis of these fast adsorption isotherms. With a view to comparing PZC obtained by the fast adsorption measurement method with the pH of the zero mobility of the oxide particles, microelectrophoretic mobility measurements of the suspended tin dioxide particles have also been made at various ionic strengths.

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Fig. 1 — Adsorption density of potential-determining ions [rH⁺ - rOH⁻] as a function of pH in NaCl as the supporting electrolyte
obtained in NaNO₃ as the supporting electrolyte. Each family of curves in both NaCl (Fig. 1) and NaNO₃ intersects at a point which corresponds to pH 4.5. This pH (4.5) may be considered as PZC of SnO₂-solution interface. No shift in PZC has been observed. This observation clearly indicates that Na⁺, NO₃⁻ and Cl⁻ have no specific affinity for the uncharged surface of SnO₂. In Fig. 2, electrophoretic mobilities of suspended SnO₂ particles have been plotted as function of pH at several ionic strengths (0.01, 0.025, 0.05 and 0.1M) maintained by NaCl. It is evident from Fig. 2 that the mobility of the suspended material becomes zero at pH 4.5 in all solutions of different ionic strengths. This isoelectric point coincides with PZC of SnO₂ solution-interface determined by fast adsorption method. Thus from the results of these two independent methods of measurement, it may be concluded that the PZC of the SnO₂-aqueous solution interface lies at pH 4.5. The PZC of the precipitated SnO₂ reported in this work is in exact agreement with the pH (4.5) of zero electrokinetic potential of hydrated SnO₂ obtained by Johanson and Buchanon. Ahmed and Maksinov used naturally occurring cassiterite and found that the PZC of the mineral-solution interface lies at pH 5.6. The difference in PZC is due to the fact that while we used synthetic SnO₂ samples whereas Ahmed and Maksinov used naturally occurring samples of SnO₂ with different surface composition.

Differential capacities of the electrical double layer in NaNO₃ are plotted as function of surface charge densities in Fig. 3. Similar plots have been obtained in NaCl as the supporting electrolyte. The general shapes of these capacity curves are very much similar to those obtained for liquid mercury-AgI (ref. 13) and ZrO₂ (ref. 2). The minimum values of the differential capacity of the double layer at SnO₂-solution interface at its point of zero charge in 0.001M NaCl and 0.001M NaNO₃ solutions are found to be 6.3 μF/cm² and 7.5 μF/cm² respectively. These values of the minimum differential capacity of the electrical double layer are in satisfactory agreement with the value (6 μF/cm²) obtained by Grahame on Hg-solution interface. Block and deBruyn found large values for the minimum differential capacity on several oxide-solution interfaces. These high values may be due to the adoption of slow adsorption technique by these investigators. The slow process complicates the study of interfacial properties towards the evaluation of PZC, differential capacities of the double layer due to the variation in surface composition. The slow process may be attributed to the anion-exchange process involving H⁺ and OH⁻ with the anions and cations of the supporting electrolytes. The slow pH drift which is commonly observed in oxide systems is due to this slow ion exchange process. This is supported by the fact that synthetic metal oxides are widely used as inorganic ion-exchangers. Metal oxides having varying capacities for ion-exchange may be prepared by controlling the experimental conditions.

We believe that reliable data on double layer characteristics such as the PZC, capacity of the double layer and surface charge densities due to potential-determining ions may be obtained (i) if the slow ion-exchange process is reduced to minimum either by using fast adsorption technique or by using samples of oxides having practically no exchange capacity or by using both and (ii) if there is no specific adsorption of foreign ions to the surface. In SnO₂ system investigated by us, we adopted fast adsorption equilibrium method. No evidence of specific adsorption of the ions of the supporting electrolytes
Fig. 4 — Interfacial free energy lowering at SnO$_2$-solution interface as a function of pH in NaNO$_3$ as the supporting electrolyte.

appears from the two sets of adsorption isotherms in the presence of NaCl (Fig. 1) and NaNO$_3$ supporting electrolytes, since their is a common intersection point in each case. Consequently, the values (6.3 µF/cm$^2$ and 7.5 µF/cm$^2$) of the minimum differential capacity of the double layer obtained by the graphical differentiation of the fast adsorption isotherms are in good agreement with the value (6 µF/cm$^2$) calculated by the Gouy-Chapman theory as modified by Grahame$^{17}$. The interfacial free energy changes ($-\Delta Y$) with respect to PZC as defined by Eq. (1) are plotted as the function of pH of the solution in Fig. 4 in the case of NaNO$_3$ supporting electrolyte. Similar plots have been obtained in NaCl. The general shapes of these curves are very much similar to electrocapillary curves with the maximum at PZC.

References