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Electrical double layer interactions between dissimilar oxide surfaces with charge regulation and Stern–Grahame layers

Derek Y.C. Chan [a,*], Thomas W. Healy [b], Tharatorn Supasiti [a], S. Usui [c]

[a] *Department of Mathematics and Statistics, The University of Melbourne, Victoria 3010, Australia*
[b] *Department of Chemical and Biomolecular Engineering, Particulate Fluids Processing Centre, The University of Melbourne, Victoria 3010, Australia*
[c] *Tohoku University, Katahira, Aoba-ku, Sendai 980-8577, Japan*

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Abstract

Models of surfaces with intrinsic ionisable amphoteric surface sites governed by the dissociation of acid–base potential determining ion species together with the capacity for the adsorption of anion and cations of the supporting electrolyte are required to describe both the results of electrokinetic and titration measurements of inorganic oxides. The Gouy–Chapman–Stern–Grahame (CGSG) model is one such model that has been widely used in the literature. The electrical double layer interaction between two dissimilar CGSG surfaces has been studied by Usui recently [S. Usui, J. Colloid Interface Sci. 280 (2004) 113] where erroneous discontinuities in the slope of the pressure–separation relation were observed. We revisit this calculation and provide a simple general methodology to analyse the electrical double layer interaction between dissimilar ionisable surfaces with ion adsorption.

Keywords: Double layer interaction; Dissimilar double layer; Charge regulation; Gouy–Chapman–Stern–Grahame model; Oxide–water interfaces; Site-binding model; Surface force

1. Introduction

The Gouy–Chapman–Stern–Grahame (CGSG) or site-binding model [1] has been used successfully to model and reconcile electrokinetic surface potential measurements of inorganic oxides with surface charge data derived from titration experiments. In this model, intrinsic amphoteric ionisable groups of the oxide surface develop a net charge in response to the solution concentration of potential determining ions or pH. In addition, the model also allows for the specific adsorption of anions and cations of the supporting electrolyte at the Stern plane. It is through the combined recognition of the ionisation of intrinsic surface groups and of ion binding in the CGSG model that made it possible to model both electrokinetic and titration data [2]. On the other hand, the CGSG model for oxides had not be been used extensively to model the electrical double layer interaction between oxide surfaces. As the state of charge of such surfaces depends on the adsorption and desorption of both potential determining ions and supporting electrolyte ions, neither the surface charge nor the surface potential are kept constant during interaction. Such surfaces are referred to as charge regulating surfaces.

Some time ago, the electrical double layer interaction between regulating amphoteric surfaces, where there is no adsorption of supporting electrolyte ions, was analysed in detail for both identical [3] and non-identical surfaces [4] using the Poisson–Boltzmann (PB) model. Numerical results for the interaction between non-identical surfaces held at different combinations of constant surface charges or surface potentials were given in [5] which generalised the earlier work that focused on the interaction between dissimilar surfaces held at constant surface potential or constant surface charge [6]. More recently, interactions between dissimilar surfaces bearing a single type of ionisable groups [7] as well as more general surface ionisations reactions [8] have been studied. Within the PB model, the interaction between flat surfaces can be obtained without having to

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[*] Corresponding author.
E-mail address: d.chan@unimelb.edu.au (D.Y.C. Chan).

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solve explicitly for the potential distribution in the electrolyte between the surfaces.

Recently, Usui [9] used the CGSG model to re-examine the electrical double layer interaction between two surfaces that have like signs but different potentials at infinite separation. The model was designed to model oxide surfaces with amphoteric. This study produced results that contained unexpected abrupt changes in slope in the pressure versus separation curves. This work suggested that previous results obtained with the Gouy–Chapman model [9] where the force of interaction can change from repulsion to attraction at some particular separation were not observed using the CGSG model of the double layer.

In this paper, we revisit the CGSG model for the electrical double layer interaction between two like charged surfaces which have potentials of the same sign but different in magnitude when they are at infinite separation. We follow the formalism developed earlier [4,5] to develop a general approach to analyse the double layer interactions under the CGSG model. We will show that the earlier calculation [9] was incorrect in suggesting that there were discontinuities in the slope of the variations of the pressure with separation.

2. Formulation

2.1. Surface potentials and charges

A schematic of the Gouy–Chapman–Stern–Grahame (CGSG) model is depicted in Fig. 1 and the we recall the main features of this model [1]. The interacting oxide surfaces develop a surface charge as a result of the dissociation of proton from amphoteric surface groups:

$$\mathrm{AH_2^+} \Leftrightarrow \mathrm{AH} + \mathrm{H^+}, \qquad \mathrm{AH} \Leftrightarrow \mathrm{A^-} + \mathrm{H^+}. \tag{1}$$

These reactions are characterised by dissociation constants K_+ and K_- according to the mass action equations

$$\frac{[\mathrm{AH}]H\exp(-e\psi_\mathrm{o}/kT)}{[\mathrm{AH_2^+}]} = K_+,$$
$$\frac{[\mathrm{A^-}]H\exp(-e\psi_\mathrm{o}/kT)}{[\mathrm{AH}]} = K_-, \tag{2}$$

where H is the bulk concentration of $\mathrm{H^+}$ ions and ψ_o is the potential at the oxide surface. In the CGSG model, similar surface complexation reactions are assumed to occur in the Stern plane for cations and anions that make up the univalent electrolyte:

$$\mathrm{AH_2^+X^-} \Leftrightarrow \mathrm{AH_2^+} + \mathrm{X^-}, \qquad \mathrm{A^-M^+} \Leftrightarrow \mathrm{A^-} + \mathrm{M^+}. \tag{3}$$

These reactions are characterised by dissociation constants K_A and K_C for the anions and cations,

$$\frac{[\mathrm{AH_2^+}]c\exp(+e\psi_\beta/kT)}{[\mathrm{AH_2^+X^-}]} = K_\mathrm{A},$$
$$\frac{[\mathrm{A^-}]c\exp(-e\psi_\beta/kT)}{[\mathrm{A^-M^+}]} = K_\mathrm{C}, \tag{4}$$

with c being the bulk (molar) concentration of univalent electrolyte $\mathrm{M^+X^-}$. The potential at the Stern plane is denoted by ψ_β (see Fig. 1).

With N_s ionisable sites per unit area of the oxide surface, the surface charge density on the oxide surface is (e is the protonic charge)

$$\sigma_\mathrm{o} = eN_\mathrm{s}\frac{[\mathrm{AH_2^+}] - [\mathrm{A^-}] + [\mathrm{AH_2^+X^-}] - [\mathrm{A^-M^+}]}{[\mathrm{AH}] + [\mathrm{AH_2^+}] + [\mathrm{A^-}] + [\mathrm{A^-M^+}] + [\mathrm{AH_2^+X^-}]}$$
$$\equiv eN_\mathrm{s}\alpha_\mathrm{o}, \tag{5}$$

and the surface charge density in the Stern layer, due to bound ions and assuming the same number of ionisable sites as at the oxide surface, is

$$\sigma_\beta = eN_\mathrm{s}\frac{[\mathrm{A^-M^+}] - [\mathrm{AH_2^+X^-}]}{[\mathrm{AH}] + [\mathrm{AH_2^+}] + [\mathrm{A^-}] + [\mathrm{A^-M^+}] + [\mathrm{AH_2^+X}]}$$
$$\equiv eN_\mathrm{s}\alpha_\beta. \tag{6}$$

The degree of ionisation at the oxide surface α_o and at the Stern plane α_β is defined by these equations with $-1 < \alpha_\mathrm{o}, \alpha_\beta < 1$.

In the CGSG model, the relations between the potential at the oxide surface ψ_o, the potential at the Stern plane ψ_β, and the potential at the boundary of the diffuse double layer ψ_d, are related to the surface charges by the capacitances (per unit area) of the inner layer K_i and outer layer K_o of the Stern region (see

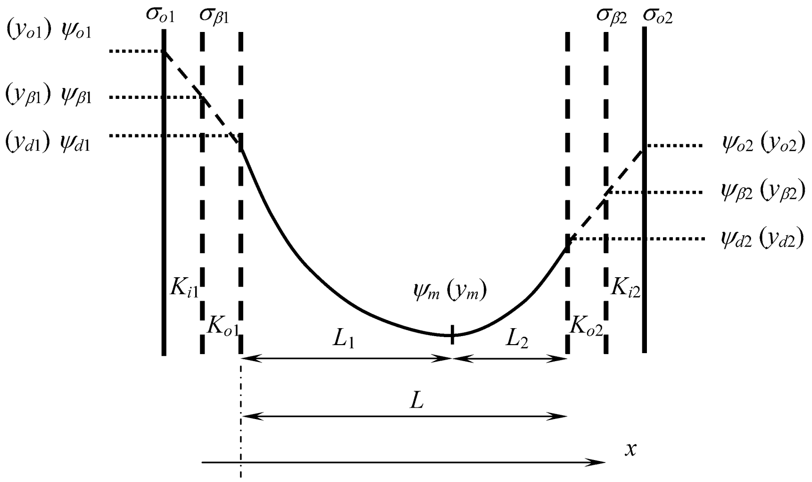

Fig. 1. Schematic diagram of the Gouy–Chapman–Stern–Grahame model of interacting oxide surfaces.