A model of the potential-dependent adsorption of charged redox-active species at the electrode surface

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ABSTRACT

A model of a non-polarizable interface is developed and considered in terms of the specific adsorption of charged redox species and the nonspecific adsorption of the supporting electrolyte. The adsorption coefficients of charged redox species depend on their charges and the potential at the inner Helmholtz plane. The adsorbed amounts of the redox species and supporting electrolyte are estimated using the Frumkin isotherm and Gouy—Chapman theory, respectively. The potential dependence of the adsorbed amount of either one or both of the oxidized and reduced forms of the redox species is maximized near its standard potential. The electrocapillary equation at a non-polarizable liquid metal—solution interface under an externally controlled potential is revisited. The derived electrocapillary equation facilitates calculating the electrocapillary curve of the non-polarizable interface based on the quantity of adsorbed ions. The electrocapillary curve calculated based on the model may have a concave part, which would indicate that the interface is thermodynamically forbidden, near the standard redox potential of the redox couple.

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1. Introduction

The adsorption of chemical species at the electrode surface is of fundamental importance in electrochemistry. However, the *in situ* observation of an electrode surface immersed in electrolyte solution is challenging for chemists. One established method of analyzing the electrode—solution interface is based on the thermodynamics described by the Gibbs adsorption isotherm [1], which relates the interfacial tension (γ) to the surface excesses (Γ_i) and chemical potentials of the chemical species i (μ_i).

When the electrochemical system is free of redox-active species, the interface between the electrode and electrolyte solution is ideally polarizable [2]. In this simple situation, the observer can independently control the electrode potential (E) and measure the value of γ. The Lippmann equation [3] relates γ at the ideally polarizable interface with the surface charge density (q^M) as

$$\left(\frac{\partial \gamma}{\partial E}\right)_{\mu_i} = q^M, \tag{1}$$

The thermodynamics of the non-polarizable interface is a classic topic for electrochemists. In this complex environment, a change in E changes the solution composition. Electrocapillary equations at the non-polarizable interface have been formulated for many situations [2,4—13]. The non-polarizable interface has three important differences compared with the ideally polarizable interface [14]. First, one fewer independent variable is needed to describe the system. Second, the sum of relative surface excesses of R and O affect the concentration dependence of γ. Third, the slope of the electrocapillary curve is no longer given by the classical Lippmann equation; that is, the slope differs from q^M. Generally, in the presence of redox species, $O + ne^- \rightleftharpoons R$, the slope of the electrocapillary curve for the non-polarizable interface is formulated as [5,10,12—14].

$$\left(\frac{\partial \gamma}{\partial E}\right)_{\mu_{i \neq 0}} = -q^M - nF\Gamma_O. \tag{2}$$

This value is called the total charge, as named by Frumkin et al. [9]. Notably, equation (2) corresponds to the situation in which the addition of the oxidized or reduced forms of the redox-active species to the solution changes the electrode potential.

Externally controlling the potential is familiar to

electrochemists as voltammetry. Under voltammetric conditions, the electrocapillary curve is automatically recorded [15–18]. However, applying equation (2) to the electrocapillary curves is difficult. Under voltammetric conditions, the electrode potential changes the ratio of the oxidized and reduced forms without changing the total concentration of the redox-active species. Therefore, another constraint—i.e., the total concentration of the redox-active species is constant—should be introduced to the electrocapillary equation to make it more convenient [7,9].

In addition, the redox reaction changes the charges of the components. The electrostatic interactions between ions and an electrode depend on their charges and the surface charge density, which is a function of the electrode potential. Therefore, at the non-polarizable interface, both the adsorption and redox reactions of redox-active ions will depend on the electrode potential. The deeply coupled nature of these reactions increase the complexity of this situation. The electrocapillary curves of mercury electrodes in the presence of thallium ions have been examined in detail by Frumkin et al. [9,19–23] The reported electrocapillary curves have a minimum located between two maxima. The cause of a minimum on the electrocapillary curve has been predicted to be adsorption of ion pairs or charged complexes [21]. However, the shape of the electrocapillary curve seems to be explained without intro-ducing new chemical species. At the liquid−liquid interface, an electro-capillary curve containing a minimum and two maxima was dis-cussed by Kakiuchi in terms of the potential-dependent adsorption and partition of ions [24,25]. This thermodynamically derived concept for the non-polarizable liquid−liquid interface will be extended to the non-polarizable electrode solution interface.

In this work, an electrocapillary equation for non-polarizable liquid metal electrodes is formulated to analyze the electro-capillary curve recorded under voltammetric conditions. Further-more, the potential-dependent adsorption of redox-active ions is introduced. The electrocapillary curves of the non-polarizable electrode under various conditions are estimated using the above concepts. The characteristics of the electrocapillary curve and the thermodynamic stability of the electrode surface are discussed based on the electrochemical instability [26].

2. Theoretical

2.1. Electrocapillary equation at a non-polarizable interface

Here, the electrocapillarity of a liquid-metal electrode contain-ing a metal g in an electrolyte solution containing a redox-active pair is investigated. The electrolyte solution contains cations j, anions k, and neutral species h. The following redox reaction is considered in this system:

$$O^m + ne^- \rightleftharpoons R^{m-n}. \tag{3}$$

The electrocapillary equation for the interface between an electrode and electrolyte solution at a constant temperature and pressure when the reference electrode is reversible to anion k' is written as [14].

$$d\gamma = -q^M dE^- - \sum_{g \neq g'} \Gamma_{gg'} d\mu_g - \sum_{j \neq j'} \frac{\Gamma_{jh'}}{\nu_{jk'}^+} d\mu_{jk'} - \sum_{k \neq k'} \frac{\Gamma_{kh'}}{\nu_{j'k}^-} d\mu_{j'k}$$
$$- \sum_{h \neq h'} \Gamma_{hh'} d\mu_h - \left[\frac{\Gamma_{j'h'}}{\nu_{j'k'}^+} - \frac{1}{z_{j'} \nu_{j'k'}^+} \sum_{k \neq k'} \Gamma_{kh'} |z_k| \right] d\mu_{j'k'}, \tag{4}$$

where E^- is the potential difference between the working electrode

and reference electrode, which is reversible to k'; z_l is the charge of ion l; μ_l is the chemical potential of component l; and $\Gamma_{lh'}$ is the relative surface excess of component l relative to that of the refer-ence component h'. The prime symbol indicates the reference component. The subscript jk represents salts consisting of j and k. The symbols ν_{jk}^- and ν_{jk}^+ represent the stoichiometric numbers of anions and cations in salt jk, respectively.

According to the electroneutrality at the electrode surface, q^M is equal to the sum of the ion charges:

$$q^M = -F \left(\sum_j z_j \Gamma_{jh'} + \sum_k z_k \Gamma_{kh'} \right). \tag{5}$$

where z_l is the charge of ion l, and $\Gamma_{lh'}$ is the surface excess of component l relative to that of reference component h'. When k' is a monovalent anion, the mass balance constraints (i.e., when the sum of the amounts of O and R is constant) are written as follows:

$$X = (x_{Ok'} + x_{Rk'})X_S, \tag{6}$$

where X_S is the total amount of all constituents in the solution phase (S), and X is the sum of the amounts of O and R. Assuming that the activity coefficients are unity, the differential of the chemical potential of Ok' ($\mu_{Ok'}$) is represented as follows:

$$d\mu_{Ok'} = RT d \ln X + nF \frac{\xi}{1+\xi} dE^-. \tag{7}$$

where ξ is a dimensionless potential defined as $\xi = \exp\left\{ -\frac{nF}{RT}(E^- - E^*) \right\}$, and E^* represents the standard redox potential. Substituting equations (5–7) into equation (4) yields equation (8), which is a more useful representation of the elec-trocapillary equation at the non-polarizable interface under vol-tammetric conditions when both O and R are cations:

$$d\gamma = -F \left\{ -\sum_{j \neq O,R} z_j \Gamma_{jh'} - \sum_k z_k \Gamma_{kh'} + \left(\frac{n\xi}{1+\xi} - m \right)(\Gamma_{Oh'} + \Gamma_{Rh'}) \right\} dE^-$$
$$- \sum_{g \neq g'} \Gamma_{gg'} d\mu_g - \sum_{j \neq j',R,O} \frac{\Gamma_{jh'}}{\nu_{jk'}^+} d\mu_{jk'} - RT(\Gamma_{Oh'} + \Gamma_{Rh'}) d\ln X$$
$$- \sum_{k \neq k'} \frac{\Gamma_{kh'}}{\nu_{j'k}^-} d\mu_{j'k} - \sum_{h \neq h'} \Gamma_{hh'} d\mu_h$$
$$- \left(\frac{\Gamma_{j'h'}}{\nu_{j'k'}^+} - \frac{1}{z_{j'} \nu_{j'k'}^+} \sum_{k \neq k'} \Gamma_{kh'} |z_k| \right) d\mu_{j'k'}. \tag{8}$$

The details of the above derivation and the electrocapillary equations for the cases of cationic O and neutral R, cationic O and anionic R, neutral O and anionic R, and anionic O and anionic R are provided in the Supporting information.

Here, the apparent surface charge density (q'), which corre-sponds to the slope of the electrocapillary curve and is defined as

$$q' = -\left(\frac{\partial \gamma}{\partial E^-} \right)_{T,p,X,\mu_{i,jk,h}} \tag{9}$$

$$= -F \sum_{j \neq O,R} z_j \Gamma_{jh'} - F \sum_k z_k \Gamma_{kh'} + F \left(\frac{n\xi}{1+\xi} - m \right)(\Gamma_{Oh'} + \Gamma_{Rh'}),$$