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(Citation)

Review of Polarography, 59(1):21-27

(Issue Date)

2013-05-31

(Resource Type)

journal article

(Version)

Version of Record

(URL)

<https://hdl.handle.net/20.500.14094/90003413>



## Electrochemical Concepts

### Theoretical Similarity between Macro- and Nano-interfaces

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Received December 4, 2012; Accepted after Peer-Review January 30, 2013

#### Abstract

A theoretical similarity has been suggested between the surface tension ( $\gamma$ ) of a macro-sized mercury electrode and the ion–solvent interaction energy at a nano-sized ion|solvent interface. In a previous theory (Osakai & Ebina, 1998), the ion–solvent 1:1 interaction energy was formulated as a quadratic function of the surface field strength ( $E$ ) of the ion. This theory has been extended to explain a near-parabolic shape of the electrocapillary curve for a mercury electrode, *i.e.*, the quadratic dependence of  $\gamma$  on the electrode potential (being roughly proportional to  $E$  at the electrode surface).

**Keywords:** surface tension, ion solvation energy, non-Bornian theory, surface field strength

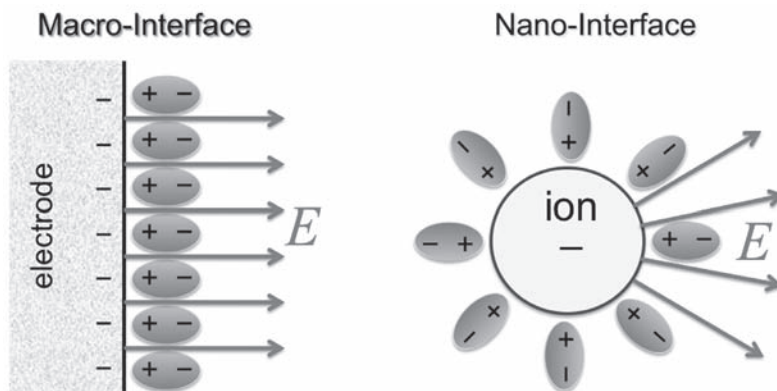
#### Introduction

The “macro-interface” appearing in the title represents a common electrode|solution or liquid|liquid interface, whereas the “nano-interface” represents a molecular-level interface between an ion and solvent molecules (see Fig. 1). In this article, it will be shown that an identical principle can be applied to understand the surface energy of macro-interfaces and the ion–solvent interaction energy of nano-interfaces, *i.e.*, ion-solvation energy.

It is well known that the potential dependence of the surface tension ( $\gamma$ ) of a mercury electrode, the so-called electrocapillary curve, shows a downward parabo-

la.<sup>1–6</sup> This shows that  $\gamma$  (with the unit being  $\text{N m}^{-1} = \text{J m}^{-2}$ ), or, the surface energy of the mercury electrode is decreased by applying a positive or negative bias potential from the point of zero charge (pzc) of the electrode. In the early 20th century, Gouy,<sup>2</sup> Frumkin,<sup>3</sup> and Butler<sup>4</sup> studied the adsorption of organic substances on the mercury electrode and discussed its dependence on the electric field at the electrode surface. In this study, it is shown that the parabolic dependence of  $\gamma$  can be explained basically by considering the dependence of the electrode–solvent interaction on the surface field strength ( $E$ ) of the electrode.

On the other hand, the surface energy of



**Fig. 1.** “Macro-interface” (electrode | solution interface) and “nano- interface” (ion | solvent interface).  $E$  shows the electric field strength at the respective interfaces.

nano-interfaces, *i.e.*, the ion-solvation energy has been understood mainly based on electrostatic models since olden times. In 1920, Born<sup>7)</sup> proposed a simple model for evaluating the ion-solvation energy ( $\Delta G_s^\circ$ ). In the classical Born model, the ion is considered as a hard sphere of a given radius ( $r$ ) immersed in a continuous medium of constant permittivity ( $\epsilon_b$ ), and then  $\Delta G_s^\circ$  is defined as the electrostatic energy for charging the ion up to  $ze$  ( $z$ , the charge number of the ion;  $e$ , the elementary charge):

$$\Delta G_s^\circ(\text{Born}) = -\frac{N_A z^2 e^2}{8\pi\epsilon_0 r} \left(1 - \frac{1}{\epsilon_b}\right) \quad (1)$$

where  $N_A$  is the Avogadro constant, and  $\epsilon_0$  the vacuum permittivity. However, the defects of the Born model have been well-known for at least 70 years and some attempts have been made to improve the model by taking into account the *dielectric saturation*, *i.e.*, the lowering of the permittivity of solvent adjacent to an ion due to the high electric field. One of

the most frequently cited modifications was proposed by Abraham and Liszi (A&L).<sup>8)</sup> In their model, the ion is surrounded by a local solvent layer of thickness  $(b - r)$  (taken as the solvent radius) and dielectric constant  $\epsilon_1$ , and then  $\Delta G_s^\circ$  is given by

$$\Delta G_s^\circ(\text{A \& L}) = -\frac{N_A z^2 e^2}{8\pi\epsilon_0 r} \left\{ \left(1 - \frac{1}{\epsilon_1}\right) \left(\frac{1}{r} - \frac{1}{b}\right) + \left(1 - \frac{1}{\epsilon_b}\right) \frac{1}{b} \right\} \quad (2)$$

On the assumption that  $\epsilon_1 = 2$ , the theoretical values of  $\Delta G_s^\circ$  were shown to agree well with the experimental values for univalent ions in various solvents including water. However, in view of Eq. (2), we notice that the assumption “ $\epsilon_1 = 2$ ” (*i.e.*,  $1/\epsilon_1 = 0.5$ ) is a great modification of the Born equation (Eq. (1)), because the  $\epsilon_1$  value is extremely small compared with the bulk permittivity  $\epsilon_b$  ( $=78.54$  for water; *i.e.*,  $1/\epsilon_b = 0.013$ ). This shows a dominant contribution of the local solvent layer to the total  $\Delta G_s^\circ$ . Ironically enough, the “modified” Born equation, proposed by A&L, insists on a significant

importance of short-range ion–solvent interactions, though the Born equation is based on the long-range electrostatic interaction.

In more recent years, Osakai and Ebina proposed a non-Bornian theory for the Gibbs energy of ion transfer at the liquid|liquid interface.<sup>9,10</sup> This theory was developed from the voltammetric study on the interfacial transfer of polyoxometalate ions of various size and ionic charge (see Refs. 11–13, and references therein). In the theory, the ion-solvation energy is formulated, not as the Bornian long-range electrostatic energy, but as short-range ion–solvent energies including *chemical* ones. The 1:1 interaction energy of an ion and an adjacent solvent is then given by a quadratic function of the surface field strength of the ion, which is expressed by

$$E = \frac{ze}{4\pi\epsilon_0 r^2} \quad (3)$$

As will be discussed below, a similar approach can be used to understand the nearly parabolic shape of the electrocapillary curve of a mercury electrode.

### Nano-interfaces

Referring to *ab initio* molecular orbital studies,<sup>14</sup> the energy for the short-range ion–solvent interaction ( $U_{\text{SR}}$ ) can be expressed by a linear combination of some interaction terms including Coulomb (COU), polarization (POL), charge-transfer (CT), and exchange (EX) terms:<sup>9,10</sup>

$$U_{\text{SR}} = U_{\text{COU}} + U_{\text{POL}} + U_{\text{CT}} + U_{\text{EX}} \quad (4)$$

The first two terms  $U_{\text{COU}}$  and  $U_{\text{POL}}$  corresponds to the empirical energy of ion–dipole and

–induced dipole interactions, being given by<sup>15</sup>

$$U_{\text{COU}} = -\mu E \langle \cos \theta \rangle \quad (5)$$

$$U_{\text{POL}} = -\frac{1}{2} \alpha E^2 \quad (6)$$

where  $\mu$  and  $\alpha$  are the dipole moment and electronic polarizability of the solvent molecule, respectively,  $\theta$  is the angle between the dipole axis and the line connecting the point dipole and point charge,  $\langle \rangle$  indicates the ensemble average, and  $E$  is the “effective” electrical field strength, which is here assumed to be given by Eq. (3).

Thus, the terms of  $U_{\text{COU}}$  and  $U_{\text{POL}}$  originate from electrostatic interactions in common with the Bornian solvation energy, which is obtained by integrating the electric field energy over all of space. However the third term  $U_{\text{CT}}$  is not electrostatic, but shows the CT interaction energy due to partial electron transfer between an ion and a primary solvent molecule. A model Hamiltonian approach<sup>13</sup> showed that  $U_{\text{CT}}$  ( $=\Delta W$  in Ref. 13) can be approximately expressed as a quadratic equation of  $E$ :

$$U_{\text{CT}} = -\xi_0 - \xi_1 E - \xi_2 E^2 \quad (7)$$

where the coefficients  $\xi_0$ ,  $\xi_1$ , and  $\xi_2$  (denoted as  $\alpha_0$ ,  $\alpha_1$ , and  $\alpha_2$  in Ref. 13) are influenced by various molecular properties of the solvent and the ion, including their electron-donating or accepting abilities.

The remaining term  $U_{\text{EX}}$  in Eq. (4) represents the non-classical repulsion term, being inherently independent of  $E$ . Finally, substituting Eqs. (5)–(7) into Eq. (4) yields

$$U_{\text{SR}} = -A - BE - CE^2 \quad (8)$$

with  $A = \xi_0 - U_{\text{EX}}$ ,  $B = \mu(\cos \theta) + \xi_1$ , and  $C = (\alpha/2) + \xi_2$ .

In the above, the ion–solvent interaction energy  $U_{\text{SR}}$  is defined for a 1:1 interaction. However, multiple primary solvent molecules adjacent to an ion can interact directly with the ion. If we assume that there is no lateral interaction between these primary solvent molecules (though somewhat unrealistic), the total short-range interaction energy, *i.e.*, the ion–solvation energy can be obtained by simply multiplying  $U_{\text{SR}}$  by the number of solvent molecules directly interacting with an ion. In our previous study,<sup>9)</sup> the standard Gibbs energy ( $\Delta G_{\text{tr}}^{\circ, \text{O} \rightarrow \text{W}}$ ) of ion transfer at the organic solvent (O)|water (W) interface, *i.e.*, the difference of the solvation energies in O and W, was well elucidated in terms of the short-range ion–solvent interactions given by Eq. (8). Our daring ignoring of the long-range electrostatic energy gave a better account of  $\Delta G_{\text{tr}}^{\circ, \text{O} \rightarrow \text{W}}$  than Bornian electrostatic models.

### Macro-interfaces

Equation (8) thus derived for the short-range interaction at the nano-size of an ion|solvent interface may be applied to describe the potential dependence of surface energy (or  $\gamma$ ) for the macro-size of a mercury electrode.

In the following, we assume the Stern model<sup>16)</sup> for the electrical double layer at a mercury electrode in the absence of specific adsorption of ions. In this simple model, the double layer is divided into two parts by the outer Helmholtz plane (OHP), only up to which the ions in the solution can approach the electrode surface. The thin layer between the OHP and the electrode surface is ion-free in the absence of specific adsorption, being called the inner layer. The layer extending beyond the

OHP is called the Gouy–Chapman (GC) space-charge layer, in which the cations and anions in the solution are distributed non-uniformly depending on the electrode potential. Based on this model, the double-layer capacity ( $C_{\text{dl}}$ ) of the electrode can be described as two capacitors in series:

$$\frac{1}{C_{\text{dl}}} = \frac{1}{C_{\text{H}}} + \frac{1}{C_{\text{GC}}} \quad (9)$$

where  $C_{\text{H}}$  is the Helmholtz or inner-layer capacity, and  $C_{\text{GC}}$  is the capacity of the space-charge layer, which can be estimated by the GC theory.<sup>6)</sup> For moderately concentrated electrolyte solutions,  $C_{\text{GC}}$  is large compared with  $C_{\text{H}}$ , so that the contribution of  $C_{\text{GC}}$  to  $C_{\text{dl}}$  is small. In the following, we consider such situation that the total double-layer capacity is governed extensively by the inner-layer contribution, *i.e.*,  $C_{\text{dl}} \approx C_{\text{H}}$ .

In the application of Eq. (8) to the mercury electrode, the number  $N$  of solvent molecules in unit surface area of an electrode should be evaluated. In a simple manner,  $N$  can be estimated by<sup>17)</sup>

$$N = 1/S = 1/V^{2/3} \quad (10)$$

where  $S$  is projected molecular area, which is related to the volume  $V$  of the solvent molecule that is assumed to be a sphere. Furthermore,  $V$  is given by the molecular weight  $M$  and density  $\rho$  of the solvent:

$$V = M/(\rho N_{\text{A}}) \quad (11)$$

Using Eqs. (10) and (11), one can estimate the  $N$  value.

Let us now assume that in a similar manner

as the ion–solvent interaction, the lateral interaction between the solvent molecules contacting with the electrode has no significant effect on the vertical electrode–solvent interaction. This assumption is more valid when the electrode potential is farther from pzc, *i.e.*, when the solvent dipoles are oriented more perpendicular to the electrode surface. Then, the short-range interaction energy per surface area (*i.e.*,  $NU_{\text{SR}}$ ) should be given by

$$NU_{\text{SR}} = -NA - NBE - NCE^2 \quad (12)$$

where  $E$  is the “effective” field strength at the electrode surface.

This interaction energy has the opposite sign of the work of adhesion ( $W_{12}$ ), *i.e.*,  $NU_{\text{SR}} = -W_{12}$ , and relates to the  $\gamma$  of a mercury electrode by the Dupré equation:<sup>18)</sup>

$$\gamma = \gamma_1 + \gamma_2 - W_{12} = \gamma_1 + \gamma_2 + NU_{\text{SR}} \quad (13)$$

where  $\gamma_1$  and  $\gamma_2$  are the surface tensions of mercury (1) and the solvent (2) against their own saturated vapors. Finally, substituting Eq. (12) to Eq. (13) yields

$$\gamma = \gamma_1 + \gamma_2 - NA - NBE - NCE^2 \quad (14)$$

For  $E > 0$ , the coefficients  $B$  and  $C$  (see the text below Eq. (8)) are both positive; and for  $E < 0$ ,  $B$  and  $C$  are negative and positive, respectively (note that  $\langle \cos \theta \rangle < 0$  and  $\xi_1 < 0$  for  $E < 0$ ). Accordingly, Eq. (14) shows that  $\gamma$  is decreased with the increase of  $|E|$ . If  $E$  is proportional to the electrode potential ( $V$ ), Eq. (14) will show a parabolic shape of the electrocapillary curve. In the following, conditions and reasons for a linear relationship between  $E$  and  $V$  will be shown.

As described above, for a mercury electrode in the absence of specific adsorption, the total double-layer capacity  $C_{\text{dl}}$  is governed extensively by the inner-layer capacity  $C_{\text{H}}$ , provided that the electrolyte concentration is moderately high. Under these conditions, we may expect a situation where  $C_{\text{H}}$  and thus  $C_{\text{dl}}$  are not very sensitive to  $V$ , at least in a certain restricted potential range.

According to Lippmann,<sup>6,19)</sup> the charge density ( $q^{\text{M}}$ ) on the electrode surface can be obtained by integrating  $C_{\text{dl}}$  from the electrode potential at the pzc ( $V_{\text{pzc}}$ ):

$$q^{\text{M}} = \int_{V_{\text{pzc}}}^V C_{\text{dl}} dV \quad (15)$$

Accordingly, when  $C_{\text{dl}}$  is independent of  $V$ ,  $q^{\text{M}}$  should be proportional to  $V$ . In practice, a roughly linear dependence of  $q^{\text{M}}$  on  $V$  was observed for a mercury electrode in the absence of specific adsorption (*e.g.*, in NaF).<sup>5)</sup>

Furthermore, Gauss’s law relates  $q^{\text{M}}$  to  $E$  just at an electrode surface:

$$E = q^{\text{M}}/\epsilon_0 \quad (16)$$

though the  $E$  value effective for the short-range electrode–solvent interaction may be lowered, to some extent, by a medium effect of the inner layer. From the relations of Eqs. (15) and (16), we can expect a linear relationship between  $E$  and  $V$ , under the conditions where  $C_{\text{dl}}$  is independent of  $V$ . It may thus be understood that Eq. (14) represents a parabolic shape of the electrocapillary ( $\gamma$  vs.  $V$ ) curve under definite conditions. It should here be stressed that Eq. (14) has been derived from a molecular viewpoint.

As described above, the conditions for the

linear dependence of  $E$  on  $V$  is that  $C_H$  is independent of  $V$ . However, the value of  $C_H$  is altered probably due to the change in the orientation of solvent molecules in the inner layer. Then,  $E$  as well as  $q^M$  would be linearly dependent on  $V$ , in either positive or negative potential region (with respect to the pzc). Accordingly, when Eq. (14) is applied to an electrocapillary curve, we should divide the curve into two portions in the positive and negative potential regions.

### Experimental Verification

As described above, the coefficients  $B$  and  $C$  in Eq. (14) are related to the electrostatic and chemical (*i.e.*, CT) properties of a solvent molecule. Accordingly, these coefficients are affected by the orientation of solvent molecules in the inner solvent layer. Now let us consider the case that the solvent is water. When the electrode is positively charged, the water dipoles would *flip up* so that the oxygen atoms are in contact with the electrode surface.<sup>20)</sup> In this situation, the water molecules tend to donate their electrons to the electrode in the CT interaction. On the other hand, when the electrode is negatively charged, the water molecules would *flop down* so that the hydrogen atoms are in contact with the electrode surface.<sup>20)</sup> A similar situation would occur for non-aqueous organic solvents.

As a result of such a consideration, we can predict that the coefficients  $B$  and  $C$  have some correlation with empirical solvent parameters,<sup>21)</sup> such as acceptor number ( $A_N$ ) and donor number ( $D_N$ ), which are the measures for the electron-pair accepting and donating abilities of a solvent. In a previous preliminary study,<sup>22,23)</sup> we measured electrocapillary curves of a dropping mercury electrode in various solvents,

including water, MeOH, EtOH, acetone, acetonitrile, 1,2-dichloroethane, tetrahydrofuran, formamide, *N*-methylformamide, and *N,N*-dimethylformamide. By correcting for a contribution of the GC space-charge layer, we determined the  $\gamma_i - E$  curves for the mercury | solvent interfaces comprising only their inner layers. The  $\gamma_i - E$  curves could be reproduced by a quadratic equation of  $E$  in accordance with Eq. (14) (though separately for positive and negative potential regions with respect to the pzc). Then, the second-order differential coefficient (*i.e.*  $NC$  in Eq. (14)) was evaluated for the respective potential regions, and the  $NC$  values for various solvents were found to have correlation with  $A_N$  or  $D_N$  (multiplied by  $N$ ).<sup>24)</sup> However, the observed correlation coefficients were not very good, even though some outlying data (*e.g.*, for formamide and *N*-methylformamide) were excluded from the regression analysis. Further experimental verification should be necessary.

### Conclusions

It has been shown that there is a theoretical similarity between the surface energy (*i.e.*,  $\gamma$ ) of a mercury electrode and the ion-solvation energy. The latter energy is mainly governed by short-range ion-solvent interactions, and the energy per primary solvent can be expressed by a quadratic equation of the surface field strength  $E$  of the ion. On the other hand, the near-parabolic shape of the electrocapillary curve for a mercury electrode, *i.e.*, the quadratic dependence of  $\gamma$  on the electrode potential, can be likewise explained by a simple double-layer model, in which the short-range interaction of the electrode with solvent molecules in the inner layer plays a dominant role in determining  $\gamma$ , and the interaction

energy shows a parabolic dependence on  $E$  at the electrode surface. This suggests a possibility that such parameters as  $\gamma$ ,  $V_{pzc}$ ,  $q^M$ , and  $C_{dl}$ , relating to electrocapillary curves, can be theoretically predicted from a molecular viewpoint.

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