



THERMODYNAMICS OF THE IDEALLY POLARIZED INTERFACE BETWEEN TWO IMMISCIBLE SOLUTIONS OF ELECTROLYTES. THE ELECTRO- CAPILLARY EQUATION AND SURFACE EXCESSES

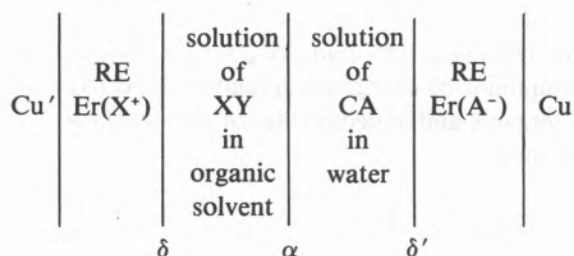
The electrocapillary equation for an ITIES is derived. Surface excesses relative to the solvent in each phase are defined and a precise definition of surface charge density on each side of the interface is presented. The residual entropy S^ is defined and a way to be calculated as a function of surface charge density is indicated.*

1 — INTRODUCTION

Polarized interfaces between two immiscible electrolyte solutions are attracting the attention of electrochemists [1-4]. The structure and properties of the electrical double layer existing at such interfaces are being investigated but, so far, no detailed thermodynamic treatment has been published. In this paper we present the electrocapillary equation for an ITIES (Interface between Two Immiscible Electrolyte Solutions) giving the proper definition of the surface charge density and all the surface excesses on both sides of the interface.

2 — THE ELECTROCAPILLARY EQUATION

To simplify, the cell considered will be one with reference electrodes reversible respectively to the cation on the organic phase and to the anion on the aqueous phase. It can be represented by



where salts XY and CA are considered to exist solely in the organic and aqueous phases respectively.

The only polarized interface is α while δ and δ' are considered non polarized and therefore the potential drop across them are exclusively determined by the activities of X⁺ (δ) and A⁻ (δ') ions. The analog of the Gibbs Duhem equation for the interphase is

$$\begin{aligned}
 -d\gamma = & S^\alpha dT - V^\alpha dp + \Gamma_X d\bar{\mu}_X + \\
 & + \Gamma_Y d\bar{\mu}_Y + \Gamma_C d\bar{\mu}_C + \Gamma_A d\bar{\mu}_A + \\
 & + \Gamma_w d\mu_w + \Gamma_O d\mu_O
 \end{aligned} \quad (1)$$

where the symbols have the following meaning

w — water, O — organic solvent, and all extensive variables are expressed per unit area of the interface and Γ_j is surface excess of species j.

The first step in the derivation is to eliminate single ion electrochemical potentials in eq. (1) using the equilibria existing in the organic and aqueous phases.

For the aqueous phase

$$d\bar{\mu}_{A^-} + d\bar{\mu}_{C^+} = d\mu_{CA}$$

or

$$\Gamma_{C^+} d\bar{\mu}_{C^+} = \Gamma_{C^+} d\mu_{CA} - \Gamma_{C^+} d\bar{\mu}_{A^-} \quad (2)$$

while for the organic phase

$$d\bar{\mu}_{X^+} + d\bar{\mu}_{Y^-} = d\mu_{XY}$$

or

$$\Gamma_{Y^-} d\bar{\mu}_{Y^-} = \Gamma_{Y^-} d\mu_{XY} - \Gamma_{Y^-} d\bar{\mu}_{X^+} \quad (2)'$$

After substitution eq. (1) becomes:

$$\begin{aligned} -d\gamma = S^\alpha dT - V^\alpha dp + (\Gamma_{X^+} - \Gamma_{Y^-}) d\bar{\mu}_{X^+} + \\ + (\Gamma_{A^-} - \Gamma_{C^+}) d\bar{\mu}_{A^-} + \Gamma_{C^+} d\mu_{CA} + \\ + \Gamma_{Y^-} d\mu_{XY} + \Gamma_w d\mu_w + \Gamma_O d\mu_O \end{aligned} \quad (3)$$

The terms $(\Gamma_{X^+} - \Gamma_{Y^-})$ and $(\Gamma_{A^-} - \Gamma_{C^+})$ represent the net amount of charge accumulated respectively on the organic and aqueous sides of the interface.

Defining

$$\sigma^w = F(\Gamma_{C^+} - \Gamma_{A^-})$$

and considering that the interphase must be electrically neutral

$$\begin{aligned} \sigma = \sigma^w = F(\Gamma_{C^+} - \Gamma_{A^-}) = -\sigma^O = \\ = -F(\Gamma_{X^+} - \Gamma_{Y^-}) \end{aligned} \quad (4)$$

These relations define the surface charge density at an ITIES and identify its value with the amounts of ions accumulated at each side of the interface.

After substitution eq. (3) becomes

$$\begin{aligned} -d\gamma = S^\alpha dT - V^\alpha dp + (\sigma/F)(-d\bar{\mu}_{X^+} - d\bar{\mu}_{A^-}) + \\ + \Gamma_{C^+} d\mu_{CA} + \Gamma_{Y^-} d\mu_{XY} + \Gamma_w d\mu_w + \Gamma_O d\mu_O \end{aligned}$$

or

$$\begin{aligned} -d\gamma = S^\alpha dT - V^\alpha dp + (\sigma/F) d\epsilon^* + \\ + \Gamma_{C^+} d\mu_{CA} + \Gamma_{Y^-} d\mu_{XY} + \\ + \Gamma_w d\mu_w + \Gamma_O d\mu_O \end{aligned} \quad (5)$$

where ϵ^* is a generalized electrochemical potential to be considered later.

It remains to eliminate in eq. (5) the chemical potentials of the solvents in each phase which requires the Gibbs-Duhem relations for each phase.

Given the miscibility of each solvent in the other such relations are

$$\begin{aligned} x_O^w d\mu_w + x_O^O d\mu_O + x_O^{XY} d\mu_{XY} + \\ + S_O dT + V_O dp = 0 \end{aligned} \quad (6)$$

$$\begin{aligned} x_w^w d\mu_w + x_w^O d\mu_O + x_w^{CA} d\mu_{CA} + \\ + S_w dT + V_w dp = 0 \end{aligned} \quad (6)'$$

where x_j^i are the molar fractions of component i in solvent j and S_j and V_j are, respectively, the molar entropies and molar volumes of the phase with solvent j .

Eqs. (6) and (6)' are a system of two equations with two unknowns, $d\mu_w$ and $d\mu_O$ the solutions of which are

$$\begin{aligned} d\mu_O = -\frac{x_w^w x_O^{XY}}{\beta} d\mu_{XY} - \frac{x_O^O x_w^{CA}}{\beta} d\mu_{CA} + \\ + \left(\frac{x_w^w S_O - x_O^w S_w}{\beta} \right) dT \end{aligned} \quad (7)$$

$$\begin{aligned} d\mu_w = -\frac{x_w^O x_O^{XY}}{\beta} d\mu_{XY} - \frac{x_O^O x_w^{CA}}{\beta} d\mu_{CA} + \\ + \left(\frac{x_O^O S_w - x_w^O S_O}{\beta} \right) dT \end{aligned} \quad (7)'$$

where

$$\beta = x_O^w x_w^O - x_w^w x_O^O \quad (8)$$

Substituting these values in eq. (5) and after rearrangement

$$\begin{aligned} -d\gamma = \Gamma_S dT - \Gamma dp + \Gamma_{C^+/w} d\mu_{CA} + \\ + \Gamma_{Y^-/O} d\mu_{XY} + q d\epsilon^* \end{aligned} \quad (9)$$

where

$$\Gamma_{C^+/w} = \Gamma_{C^+} + \frac{\Gamma_w x_O^O - \Gamma_O x_w^O}{x_O^w x_w^O - x_w^w x_O^O} x_w^{CA} \quad (10)$$

$$\Gamma_{Y^-/O} = \Gamma_{Y^-} + \frac{\Gamma_O x_w^w - \Gamma_w x_O^w}{x_O^w x_w^O - x_w^w x_O^O} x_O^{XY} \quad (11)$$

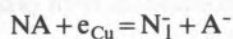
are the surface excesses in the aqueous phase relative to the water and in the organic phase relative to the organic solvent and

$$\Gamma_S = S^\alpha + \frac{\Gamma_w x_O^O - \Gamma_O x_O^w}{x_O^w x_w^O - x_w^w x_O^O} S_w + \frac{\Gamma_O x_w^w - \Gamma_w x_w^O}{x_O^w x_w^O - x_w^w x_O^O} S_O \quad (12)$$

is the surface excess of entropy.

It is needed now to clarify the meaning of the generalized electrochemical potential ϵ_-^* . Let us consider the equilibrium existing at each reference electrode assumed to be

i) in the aqueous phase



and

$$d\bar{\mu}_{A^-} = d\mu_{NA} + d\bar{\mu}_{e_{Cu}} - d\mu_N$$

ii) in the organic phase



and

$$d\bar{\mu}_{X^+} = d\mu_X - d\bar{\mu}_{e_{Cu'}}$$

Replacing these values in eq. (9), it becomes

$$-d\gamma = \dots + (\sigma/F) \{ (-d\mu_X - d\mu_{NA} + d\mu_N) + (d\bar{\mu}_{e_{Cu'}} - d\bar{\mu}_{e_{Cu}}) \} + \dots \quad (13)$$

or

$$-d\gamma = \dots (\sigma/F) (dK + (d\bar{\mu}_{e_{Cu'}} - d\bar{\mu}_{e_{Cu}})) \quad (14)$$

If ϕ'' and ϕ' are the inner potentials of the two chemically identical copper wires connected to both reference electrodes then

$$d\bar{\mu}_{e_{Cu'}} - d\bar{\mu}_{e_{Cu}} = F(d\phi'' - d\phi') = F dE_-^* \quad (15)$$

where E_-^* refers to the potential of the right hand side of the cell with respect to the left hand side. At constant temperature $dK=0$ because it only refers to solid phases of the reference electrodes.

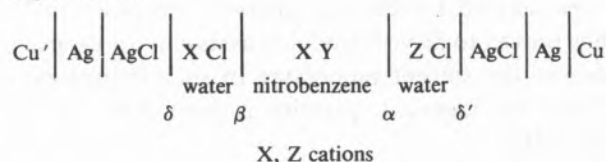
The generalized potential ϵ_-^* is, therefore, given by

$$\epsilon_-^* = E_-^* + \frac{\mu_N - \mu_{NA} - \mu_X}{F} \quad (16)$$

3 — PHYSICAL IMPLICATIONS OF THE ELECTROCAPILLARY EQUATION

As it can be noted in eq. (9-12) the relations for an ITIES are similar to those obtained for the mercury-solution interface. Determination of the surface excess of an ion in one of the phases requires the use of a reference electrode reversible to the ion of opposite charge in the same phase, keeping constant the activity of the salt on the other phase. This obviously means to keep constant the potential of the reversible reference electrode in the other phase. It is clear that any choice of a reference electrode reversible to an ion in solution is possible and there are 4 possible combinations.

However it is more usual to use an Ag/AgCl reference electrode in both sides of the interface as represented



The reference electrode on the right hand side is reversible to Cl^- anion present in the aqueous phase and thus, keeping constant the composition of the organic phase and the potential at the other reference electrode it is possible to determine the surface excess of ion Z^+ .

To make the potential drop across interface β with a Nernstian response to the activity of X^+ in the organic phase requires the use of appropriate conditions which are not in the scope of this paper.

It must be emphasized that the relative surface excesses of the ions each phase are effected by the degree of miscibility of both solvents. When such miscibility is very small eq. (10,11) can be approximated by

$$\Gamma_{C^+/w} = \Gamma_{C^+} + \frac{x_w^{CA}}{x_w^w} \Gamma_w$$

$$\Gamma_{Y^-/O} = \Gamma_{Y^-} + \frac{x_O^{XY}}{x_O^O} \Gamma_O$$

which are the values found for the case of two completely immiscible phases.

It is easy to show that the charge densities on each side of the interphase defined as

$$\sigma^w = \Gamma_{C^+} - \Gamma_{A^-}$$

and

$$\sigma^O = \Gamma_{X^+} - \Gamma_{Y^-}$$

are also given by

$$\sigma^w = \Gamma_{C^+/w} - \Gamma_{A^-/w}$$

and

$$\sigma^O = \Gamma_{X^+/O} - \Gamma_{Y^-/O}$$

These quantities are easily generalised for any number of cations or anions adsorbed.

4 — THE ENTROPY OF FORMATION OF THE ITIES

A non-thermodynamic excess of entropy, S^* has been defined for the Hg/solution interface which has proved to be very useful in assessing the properties of the solvent monolayer in such interphases [5-8]. An identical quantity is here defined for an ITIES.

S^* is defined as the residual

$$S^* = \Gamma_S - \sum_i \Gamma_{i/w} \dot{s}_w^i - \sum_j \Gamma_{j/O} \dot{s}_O^j \quad (17)$$

where Γ_S is the thermodynamic surface excess of entropy, $\Gamma_{i/w}$ and $\Gamma_{j/O}$ are relative surface excesses as defined by eqs. (10) and (11) and \dot{s}_w^i and \dot{s}_O^j are respectively the partial molar entropies of components i and j and in the aqueous and organic phases.

Using the definition of surface charge densities eq. (17) becomes

$$S^* = \Gamma_S - (\sigma/F) \dot{s}_w^+ - \Gamma_{-/w} \dot{s}_w^{\text{salt}} + (\sigma/F) \dot{s}_O^+ - \Gamma_{-/O} \dot{s}_O^{\text{salt}} \quad (18)$$

where \dot{s}_j^{salt} is the partial molar entropy of the salt existing in the phase of solvent j .

After rearranging eq.(18) becomes

$$S^* = \Gamma_S - \sigma/F (\dot{s}_w^+ - \dot{s}_O^+) - \Gamma_{-/w} \dot{s}_w^{\text{salt}} - \Gamma_{-/O} \dot{s}_O^{\text{salt}} \quad (19)$$

or in general terms

$$S^* = \Gamma_S - \sigma/F (\dot{s}_w^{\pm} - \dot{s}_O^{\pm}) - \Gamma_{\pm/w} \dot{s}_w^{\text{salt}} = \Gamma_{\pm/O} \dot{s}_O^{\text{salt}} \quad (20)$$

where the superscripts in \dot{s} correspond in the same order to the subscripts in Γ .

If the reference electrodes used are as assumed in part 2, eq.(20) takes the form

$$S^* = \Gamma_S - \sigma/F (\dot{s}_w^+ - \dot{s}_O^-) - \Gamma_{-/w} \dot{s}_w^{\text{salt}} + \Gamma_{+/O} \dot{s}_O^{\text{salt}} \quad (21)$$

Substituting in eq.(9) the value of Γ_S as obtained from eq.(21) it becomes

$$-d\gamma = (S^* + \sigma/F (\dot{s}_w^+ - \dot{s}_w^-) - \Gamma_{-/w} \dot{s}_w^{\text{salt}} + \Gamma_{+/O} \dot{s}_O^{\text{salt}})dT + \sigma d\epsilon^+ + \Gamma_{-/w} d\mu_w^{\text{salt}} + \Gamma_{+/O} d\mu_O^{\text{salt}} \quad (22)$$

Therefore at constant composition in both phases eq.(22) can be written

$$-d\gamma = (S^* + \sigma/F (\dot{s}_w^+ - \dot{s}_w^-))dT + q d\epsilon^+ \quad (23)$$

because

$$d\mu_w^{\text{salt}} = -\dot{s}_w^{\text{salt}} dT$$

and

$$d\mu_O^{\text{salt}} = -\dot{s}_O^{\text{salt}} dT$$

Eq.(23) establishes the route to obtain values of S^* directly from the temperature coefficients of the interfacial tension, or indirectly through the temperature coefficients of the differential capacities. The meaning of S^* in the case of an ITIES is not as simple as in the case of two completely immiscible phases and is given by

$$S^* = \Gamma_w (\dot{S}_\alpha^w - \dot{s}_w^w) + \Gamma_O (\dot{S}_\alpha^O - \dot{s}_O^O) + \Gamma_w^- (\dot{S}_\alpha^- - \dot{s}_w^-) + \Gamma_w^+ (\dot{S}_\alpha^+ - \dot{s}_w^+) + \Gamma_O^- (\dot{S}_\alpha^- - \dot{s}_O^-) + \Gamma_O^+ (\dot{S}_\alpha^+ - \dot{s}_O^+) - b x_O^w (\dot{s}_w^w - \dot{s}_w^O) - a x_w^O (\dot{s}_O^O - \dot{s}_w^O)$$

where

$$b = \frac{\Gamma_O x_w^w - \Gamma_w x_O^O}{x_O^w x_w^O - x_w^w x_O^O}$$

$$a = \frac{\Gamma_w x_O^O - \Gamma_O x_w^w}{x_O^w x_w^O - x_w^w x_O^O}$$

Γ_j^{\pm} are the surface excesses of the anion or cation existing in solvent j .

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RESUMO

Termodinâmica da interface idealmente polarizável entre duas soluções imiscíveis de eletrólitos.

A equação electrocapilar e os excessos superficiais.

Apresenta-se a equação electrocapilar para uma interface idealmente polarizada entre duas soluções imiscíveis de eletrólitos. Definem-se os excessos superficiais relativos ao solvente de cada fase assim como a densidade de carga superficial em ambos os lados da interface. Define-se uma entropia residual S^* e estabelece-se uma forma do seu valor ser calculado em função da densidade superficial da carga.