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Does electrical double layer formation lead to salt exclusion or to uptake?

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When electric double layers are formed, cases have been reported where this formation involves expulsion of electrolyte into the solution and cases in which electrolyte is absorbed from the solution. Both situations are experimentally and theoretically documented, but they cannot be simultaneously correct. In this paper it is shown that this seeming conflict finds its cause in the way the double layer is formed: expulsion for double layers forming spontaneously by ion adsorption from the solution, but uptake when the double layer is formed by an external field. A thermodynamic analysis is presented.

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I. PROBLEM STATEMENT

In the scientific literature seemingly contradictory information can be found on the sign of the salt exchange with the surroundings (uptake or expulsion) when electric double layers are formed.

On the one hand, there is the familiar Donnan equilibrium, according to which charging of a polyelectrolyte or colloid leads to salt expulsion, i.e., to an increase of electroneutral electrolyte in the dialysate from which the sol is separated by a semipermeable membrane [1–3]. This phenomenon is well established, both theoretically via double layer thermodynamics [4] and experimentally by direct measurements. A telling illustration of the latter category is that of salt sieving by soils, which is the environmental precursor of reverse osmosis through plugs or membranes.

On the other hand, formation of double layers by applying an electric field across two polarizable metal electrodes immersed in an electrolyte leads to electrolyte uptake. For this phenomenon also compelling evidence is available, both experimentally and theoretically. For a recent contribution, see Ref. [5], where other references can be found. So there seems to be a problem of principle: double layers cannot simultaneously absorb and expel electrolyte.

In this paper it is shown that this is only a seeming controversy which is caused by the way in which the double layer is formed: by applying an external force, or spontaneously.

II. PRINCIPLE OF THE SOLUTION OF THE PROBLEM

As a first step to discriminate between the two different ways of charging double layers it is important to realize two basic features.

(i) The surface charge on the colloidal particles or electrodes is partly compensated by an excess of counterions and a deficit of co-ions. Stated otherwise, positive adsorption of counterions must take place together with negative adsorption of co-ions.

(ii) Double layers as a whole are always electroneutral. Hence, in the quest for a basic thermodynamic analysis it must therefore be possible, if not mandatory, to formulate the various ionic uptakes and releases in terms of overall electroneutral entities only.

Regarding the difference between the two charging mechanisms, it is mandatory to recall the difference between the natures of the charge-forming processes. In the ideal case, in order to apply an external potential difference between two metal electrodes, these interfaces should be *polarizable*, implying that the applied potential does not leak away by Faradaic currents (there are no interfacial redox reactions, etc.). For the sake of argument, below we shall assume this to be the case. On the other hand, colloidal particles in aqueous electrolyte solutions acquire their surface charge by preferential uptake of certain ionic species, say H^+ and OH^- ions for oxidic materials. Such interfaces are continually in adsorption-desorption equilibrium with the solution. We denote such interfaces as *relaxed*. Henceforth we shall assume such systems to be ideally relaxed. In the literature examples can be found of interfaces that are partially polarizable and partially relaxed, so-called *amphifunctional* interfaces [6]. We shall not consider these here. On the basis of these considerations one can qualitatively understand the sign difference between the salt uptakes of the two systems.

For polarizable electrodes, the driving force for double layer formation is external and of electric origin. One of the electrodes attains an excess of electrons, the other a deficit. To neutralize the resulting surface charges the former needs extra cations, the latter extra anions. These are absorbed from the surroundings. Qualitatively, this explains the trend of electrolyte uptake. However, for quantification this conclusion has to be qualified: surface charges, imposed on an electrode, are not solely compensated by counterions absorbed from the solution, but also by negative adsorption of co-ions, leading to electrolyte expulsion [4]. For very low surface potentials these two contributions are equal, hence in that case there is no overall expulsion or uptake by electrolyte. However, in the usual situation of not-so-low potentials, which we shall now consider, the positive adsorption of counterions outweighs the negative adsorption of coions, confirming the general uptake found by Bazant *et al.* [5].

For relaxed interfaces, the driving force for double layer formation is intrinsic and of a chemical origin. In these systems, positive and negative adsorption also takes place but in practice the situation is more complex because the solution invariably contains two electrolytes. The first electrolyte contains ions that strongly chemically adsorb on the surface and are consequently responsible for the formation of the surface charge. Such ions are called *charge determing* (CD). Examples are protons (H^+) and hydroxyl ions (OH^-) for oxidic surfaces. They are administered as acids (HNO_3) and/or bases (KOH). Automatically KNO_3 may be formed. The concentration in the solution of these electrolytes is mostly low, say less than $10^{-3}M$. The double layer resulting from such an addition is not well defined, because part of the added acid, or base, is also negatively adsorbed. For instance, when to an oxide HNO_3 is added of which the protons adsorb, the countercharge is partly made up of the accompanying NO_3^- ions, partly by NO_3^- stemming from KNO_3 that may have been formed, and partly by negative adsorption of nonadsorbed protons, acting as co-ions. In practice, this situation is always better defined by adding an *indifferent carrier electrolyte*, KNO_3 in this case. Electrolytes are called indifferent when they do not contain charge-determining ions, i.e., their ions are only electrostatically attracted by, or repelled from, the charged surface. They behave as a carrier electrolyte if their concentration strongly exceeds that of the acid and/or base. Consequently, the amounts of counterions and co-ions are dominated by the second electrolyte (KNO_3 in this case). So, under the usual practical conditions, from a positively charged oxide (resulting from adsorption of H^+ ions), K^+ ions are repelled, which is observed as an increase of the KNO_3 concentration beyond the double layer; from a negative surface (by OH^- adsorption) NO_3^- is repelled, leading to the same result. In conclusion, charging of relaxed double layers by CD ion adsorption always leads to electrolyte expulsion, just the other way around from what occurs when charging by application of an external field across two electrodes. This is basically the physical background of the observed "contradiction."

Elaboration of these principles requires a double layer model. However, it is also possible to do so on a higher level of abstraction by thermodynamic arguments, which do not require such a model.

III. THERMODYNAMIC FOUNDATIONS

Consider the simplest systems compatible with the present issue: either an ideally polarizable (P) or fully relaxed (R) interface in an aqueous solution containing HNO_3, KOH, and an excess of KNO_3. None of the ionic species adsorbs specifically on the P electrode, but strong specific adsorption of H^+ and OH^- ions does take place at the R surface and this is responsible for the surface charge σ^0. By "specific adsorption" is meant adsorption by chemical forces. When such forces are absent ions can only electrostatically interact with a charged surface. Because of the chemical equilibrium $HNO_3 + KOH \rightleftarrows KNO_3 + H_2O$,

$$d\mu_{HNO_3} + d\mu_{KOH} = d\mu_s + d\mu_w \quad (P,R) \tag{1}$$

where s and w stand for salt (KNO_3) and water, respectively. At p, T fixed μ_w is also fixed, so $d\mu_w = 0$ and

$$d\mu_{HNO_3} + d\mu_{KOH} = d\mu_s \quad (P,R). \tag{2}$$

According to Gibbs [7], the excess Gibbs energy, also known as Gibbs free energy or free enthalpy, per unit area, G_a^σ, is, for a relaxed interface, related to the surface excesses of Γ_i of all electroneutral components i in the system,

$$dG_a^\sigma = -\sum_i \Gamma_i d\mu_i \quad (R). \tag{3}$$

For fluid interfaces, G_a^σ is the interfacial tension; the quantities Γ_i (in moles per unit area) are also known as surface concentrations.

For a polarized interface an additional electric term is needed, caused by the applied field:

$$dG_a^\sigma = \psi^0 d\sigma^0 - \sum_i \Gamma_i d\mu_i \quad (P), \tag{4}$$

where σ^0 is the (electron) surface charge and ψ^0 the potential applied. The extra term is positive: the charging of the electrodes increases the Gibbs energy.

Reference states have to be specified. Following Gibbs [7] all surface excesses Γ_i are referred to the major component, water. This means that the Gibbs dividing plane is located at a position where $\Gamma_w \equiv 0$. As for low mole fractions of all dissolved substances ($x_i \ll x_w$) this plane virtually coincides with the physical solid-water interface, we may identify all Γ_i's to their analytical excesses and ignore the $\Gamma_w d\mu_w$ term in Eqs. (3) and (4). With respect to the reference point for the charge, for the P case we assume that $\sigma^0 = 0$ in the absence of the field. At that point the potential drop across the interface is probably nonzero, and not known, but $d\psi^0$ is measurable. One of the electrodes becomes positive, the other negative by polarization. For the R case the point of zero charge is that pH in the solution for which $\Gamma_{H^+} = \Gamma_{OH^-}$ at given μ_s. In the presence of carrier electrolyte this zero point is measured as $\Gamma_{HNO_3} = \Gamma_{KOH}$.

Identifying the various components i, for the R case

$$dG_a^\sigma = -\Gamma_{HNO_3} d\mu_{HNO_3} - \Gamma_{KOH} d\mu_{KOH} - \Gamma_s d\mu_s. \tag{5}$$

Equation (1) can be used to eliminate either $d\mu_{KOH}$ or $d\mu_{HNO_3}$. Choosing the former,

$$dG_a^\sigma = -(\Gamma_{HNO_3} - \Gamma_{KOH}) d\mu_{HNO_3} - (\Gamma_{KOH} + \Gamma_s) d\mu_s \quad (R), \tag{6}$$

where $\Gamma_{HNO_3} - \Gamma_{KOH}$ may be identified as σ^0/F and $\Gamma_{KOH} + \Gamma_s$ as the charge contributed by the K^+ ion, σ_{K^+}/F. Here F is the Faraday, equal to eN_{Av} where N_{Av} is Avogadro's number and e the elementary charge. For a negative surface $\sigma_{K^+} > 0$; for a positive one $\sigma_{K^+} < 0$ (expulsion). Had we eliminated $d\mu_{HNO_3}$, we would have obtained the corresponding equation with $\sigma_{NO_3^-}$; the two are equivalent and related by $\sigma^0 + \sigma_{K^+} + \sigma_{NO_3^-} = 0$, because of overall electroneutrality. Hence,

$$dG_a^\sigma = -\frac{\sigma^0}{F} d\mu_{HNO_3} - \frac{\sigma_{K^+}}{F} d\mu_s \quad (R). \tag{7}$$

We continue to consider the situation that $c_{KNO_3} \gg c_{HNO_3}, c_{KOH}$. Then, in Eq. (4) the electrolyte contribution is the only adsorption term left,

$$dG_a^\sigma = \psi^0 d\sigma^0 - \Gamma_s d\mu_s \quad (P) \tag{8}$$

whereas in Eq. (7) $d\mu_{\mathrm{HNO_3}} = d\mu_{\mathrm{H^+}} = -2.303RT\, d(p\mathrm{H})$ $(R = N_{\mathrm{Av}} k_B)$ so that

$$dG_a^\sigma = -\frac{2.303RT}{F}\sigma^0 d(p\mathrm{H}) - \frac{\sigma_{\mathrm{K^+}}}{F} d\mu_s \quad (R). \tag{9}$$

Equations (8) and (9) must now be compared with respect to the sign of the salt absorption. In practice, for polarized interfaces mostly Γ_s is measured as a function of an applied potential, so that Eq. (8) should be transformed into

$$d\xi = -\sigma^0 d\psi^0 - \Gamma_s d\mu_s \quad (P). \tag{10}$$

Hence,

$$\left(\frac{d\Gamma_s}{d\psi^0}\right)_{\mu_s} = \left(\frac{d\sigma^0}{d\mu_s}\right)_{\psi^0} \quad (P), \tag{11}$$

stating that the change of the surface concentration with the applied potential equals the change of the surface charge with the electrolyte activity at fixed potential. The latter derivative is always positive: for positive potentials $(d\psi^0 > 0)$ σ^0 becomes more positive if μ_s is increased because of better screening, whereas for negative $d\psi^0$ also $d\sigma^0/d\mu_s < 0$ because σ^0 becomes more negative. This is in line with the findings of Bazant *et al.* [5]. We note that the thermodynamics can be elaborated to also account for the negative adsorption part that makes the uptake zero (but never negative) close to the zero point.

For the reversible situation, from Eq. (9)

$$d\xi' = -\frac{2.303RT}{F}(p\mathrm{H})d\sigma^0 - \frac{\sigma_{\mathrm{K^+}}}{F} d\mu_s \quad (R), \tag{12}$$

$$2.303RT\left(\frac{d\sigma_{\mathrm{K^+}}}{d\sigma^0}\right)_{\mu_s} = -\left(\frac{d(p\mathrm{H})}{d\mu_s}\right)_{\sigma^0} \quad (R). \tag{13}$$

Here the right-hand side is experimentally accessible from titration curves; see the sketch in Fig. 1. For $\sigma^0 > 0$, $d(p\mathrm{H})/d\mu_s > 0$; for $\sigma^0 < 0$ it is the other way around. For positive $d\sigma^0$ it therefore follows that $d\sigma_{\mathrm{K^+}} < 0$, i.e., $\mathrm{K^+}$ is negatively adsorbed, meaning that the salt is expelled. In this situation $\mathrm{NO_3^-}$ is positively adsorbed as $\mathrm{HNO_3}$. On the other side of the point of zero charge $\mathrm{K^+}$ is positively adsorbed as KOH, whereas the $\mathrm{NO_3^-}$ is negatively adsorbed, also as $\mathrm{KNO_3}$.

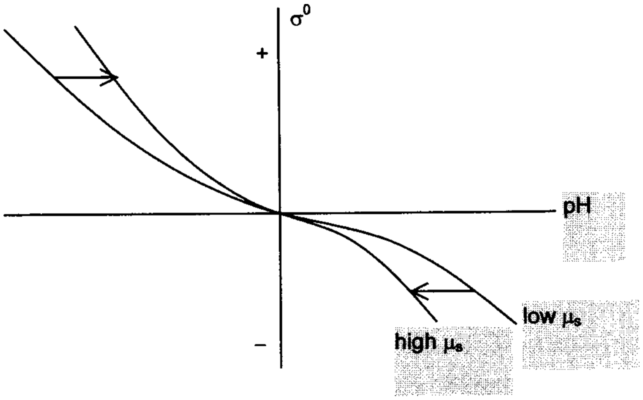

FIG. 1. Trend of the titration charge on oxides for different electrolyte contents.

IV. CONCLUSION

Double layers formed by an externally applied potential *absorb* electroneutral electrolyte, whereas double layers formed spontaneously by adsorption of charge-determining ions *expel* electrolyte.

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