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ON THE CHARGE TRANSFER IN THE PROCESS OF ADSORPTION AT THE ELECTRODE/SOLUTION INTERFACE

REMARKS ON THE PAPER "EXPERIMENTAL DETERMINATION AND INTERPRETATION OF THE ELECTROSORPTION VALENCY γ" BY J. SCHULTZE AND K. VETTER

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In recent years the attention of electrochemists has been attracted by the problem of quantitative estimation of the role of charge transfer in the chemisorption of substances at the electrode/solution interface[1–9].

For this purpose Vetter and Schultze[7–9] suggest using the quantity γ, which in the case of chemisorption of the particle i is determined by the relation

$$\gamma = \left(\frac{\partial \mu_i^{(h)}}{\partial \psi_u}\right)_{\Gamma_i^{(1)}} = -\left(\frac{\partial \varepsilon}{\partial \Gamma_i^{(1)}}\right)_{\psi_u} \tag{1}$$

where $\mu_i^{(h)}$ is the chemical potential of the particle i on the outer Helmholtz plane, related to the chemical potential in the bulk solution by the equation $\mu_i^{(h)} = \mu_i - z_i F \psi_0$; z_i is the charge of the particle i with account taken of the sign; ψ_u and ψ_0 are the potential differences in the compact and diffuse layers, respectively; $\Gamma_i^{(1)}$ is the specific adsorption of the component i (in the compact layer); ε is the electrode charge.

In refs. 7–9 the quantity $\Gamma_i^{(1)}$ is called "the electrosorption" and the quantity γ "the electrosorption valency". We do not think these terms to be quite appropriate. In fact, according to the definition of "electrosorption" in refs. 7–9, the adsorption of, say, Na^+ ions on mercury at -1.5 V is not "electrosorption", whereas the adsorption of butyl alcohol or higher fatty acids at the mercury/solution interface should be considered as such, although in this case, while the electrode charge is not too large, the behavior of the adsorbed layers is quite similar to that of adsorbed layers at the interface with air. The term "the electrosorption valency" can hardly be applied when the adsorption at the mercury surface of neutral aliphatic organic or uncharged inorganic substances is considered.

To our mind, it would be more correct to call γ "the formal coefficient of charge transfer" since, as was shown[7–9], it takes account not only of the true charge transfer during adsorption, but also of a number of other factors associated with the changes in the surface layer structure.

Passing to the actual problem discussed by Vetter and Schultze, let us consider under what conditions the second equation in relation (1) is valid. According to

Vetter and Schultze[7–9], relation (1) is a thermodynamic one and therefore should be applicable to any equilibrium system. Let us show that this conclusion is of limited validity considering two very simple cases, namely that of an anion adsorbed on an ideal polarized electrode (the cation being surface inactive) and that of an organic molecule.

In the first case, for an electrolyte solution of type $C_{\nu_+}A_{\nu_-}$ the basic equation of electrocapillarity can be written in the form[10,11]:

$$-d\sigma = \varepsilon d\varphi_+ + (\Gamma_-/\nu_-)d\mu_{C_{\nu_+}A_{\nu_-}} \tag{2}$$

where the electrode potential φ_+ is measured against an electrode reversible with respect to the cation C^{z+} and the surface excess of the anion A^{z-} (Γ_-) is referred to the plane defined by the condition $\Gamma_{H_2O}=0$. From the property of the total differential of the reversible surface work $d\sigma$ in eqn. (2) we can obtain the rigorously thermodynamic relation

$$\left(\frac{\partial \mu_{C_{\nu_+}A_{\nu_-}}}{\partial \varphi_+}\right)_{\Gamma_-} = -\left(\frac{\partial \varepsilon}{\partial \Gamma_-}\right)_{\varphi_+} \tag{3}$$

which however is different from eqn. (1). Equation (3) was first given by Parsons (see ref. 12, eqn. (4)). To obtain eqn. (1) from eqn. (3) it is necessary to make the following nonthermodynamic assumptions:

(1) In the layer adjacent to the electrode it should be possible to draw a plane (the outer Helmholtz plane) separating the "inner" (compact) layer, containing only specifically adsorbed anions, from the outer (diffuse) layer, whose structure is determined only by the sum of the charges of the electrode surface and of the inner layer.

(2) The solution is dilute, so that the plane $\Gamma_{H_2O}=0$ is located so close to the metal surface that the total anion excess can be represented as the sum

$$\Gamma_- = \Gamma_-^{(1)} + \Gamma_-^{(2)} \tag{4}$$

where $\Gamma_-^{(1)}$ is the anion excess in the compact layer, $\Gamma_-^{(2)}$ that in the diffuse layer.

(3) The properties of the diffuse layer are determined only by the potential at the outer Helmholtz plane and by the concentration of ions. Then

$$-d\sigma^{(2)} = -\varepsilon_2 d\varphi_+^{(2)} + (\Gamma_-^{(2)}/\nu_-)d\mu_{C_{\nu_+}A_{\nu_-}} \tag{5}$$

where $\sigma^{(2)}$ is the reversible work of formation of a unit surface of a hypothetical electrode with the charge $\varepsilon+\varepsilon_1$, on which there is already no specific adsorption, ε_2 is the charge of the diffuse layer at this electrode and $\varphi_+^{(2)}$ the electrode potential measured against the same reference electrode. Then

$$d\varphi_+^{(2)} = d\psi_0 - \frac{d\mu_+}{z_-F} = -\frac{d\mu_+^{(h)}}{z_+F} \tag{6}$$

In virtue of the electroneutrality of the surface layer

$$-\varepsilon_2 = \varepsilon + \varepsilon_1 = \varepsilon + z_-F\Gamma_-^{(1)} \tag{7}$$

Subtracting eqn. (5) from eqn. (2) and taking account of formulas (4), (6) and (7), as well as of the general relations

$$d\mu_{C_{\nu_+}A_{\nu_-}} = \nu_+ d\mu_+ + \nu_- d\mu_- = \nu_+ d\mu_+^{(h)} + \nu_- d\mu_-^{(h)} \text{ and } z_+\nu_+ + z_-\nu_- = 0$$

we obtain

$$-d\sigma^{(1)} = \varepsilon d\psi_u - \varepsilon_1 d\varphi_+^{(2)} + (\Gamma_-^{(1)}/\nu_-)d\mu_{C_{\nu_+}A_{\nu_-}} =$$
$$= \varepsilon d\psi_u + (z_-/z_+)d\mu_+^{(h)}\Gamma_-^{(1)} + \Gamma_-^{(1)}d\mu_-^{(h)} + (\nu_+/\nu_-)\Gamma_-^{(1)}d\mu_+^{(h)} =$$
$$= \varepsilon d\psi_u + \Gamma_-^{(1)}d\mu_-^{(h)} \qquad (8)$$

From eqn. (8), in virtue of the property of the total differential, it is easy to obtain the relation of Vetter–Schultze (1) for the specific anion adsorption. However, as we have seen, this relation is valid only if the above-mentioned nonthermodynamic assumptions are complied with. This is the case when Grahame's model[13] can be used. It is just for this reason that when using this theory for calculation of ψ_0, ψ_u and $\Gamma_-^{(1)}$, Vetter and Schultze[9] found eqn. (1) to be in good agreement with the experimental data on anion adsorption on a mercury electrode. In the general case, however, it is necessary to take into consideration the effect of the compact-layer ions on the diffuse-layer structure. Thus, in interpreting the kinetics of many electrochemical reactions, *e.g.* such as the reactions of electroreduction of anions[14,15], ionic pairs are assumed to be formed between the specifically adsorbed anions and cations of the solution. Under these conditions, the diffuse layer properties should depend on the compact layer structure. In this case and generally when account is taken of the discrete nature of the charges in the diffuse layer, eqn. (5) and hence eqn. (1) are invalid. Similar difficulties arise in the case of simultaneous specific adsorption of cations and anions, for example, in $TlNO_3$ solutions[16,17].

In the case of adsorption of neutral organic molecules $-\varepsilon_2 = \varepsilon$, $\mu_{org}^{(h)} = \mu_{org}$, but the breaking up of the total surface excess of Γ_{org} in sufficiently dilute solutions of organic substances into $\Gamma_{org}^{(1)}$ and $\Gamma_{org}^{(2)}$ is practically not feasible. Therefore, in order to use relation (1), in this case it is necessary to make another nonthermodynamic assumption, namely that the whole experimentally determined surface excess of organic substance Γ_{org} is localized within one monolayer located between the electrode surface and the outer Helmholtz plane. This assumption seems to be valid for relatively small organic molecules which at the same time possess a considerable surface activity (*e.g.* n-butanol, phenol). At small surface coverages, large organic molecules will become embedded in the diffuse layer and thus invalidate this condition, affecting simultaneously the diffuse-layer structure. On the other hand, the surface excess of organic substances having a small surface activity will be distributed in a rather thick surface layer, as was first demonstrated for the solution/air interface[18]. A similar phenomenon is observed in the case of adsorption on mercury of ethyl alcohol from aqueous solutions[19]. Just as for anions adsorption, relation (1) will be violated in the presence of specific interaction of adsorbed organic molecules with the diffuse-layer ions. The data on the influence of pyridine adsorption on the surface excess values of K^+ and Cl^- at large negative charges of a mercury electrode[20] can serve as an example of such an interaction. Finally, at concentrations close to saturation of the solution, polylayers are formed at the mercury/solution interface[21], which also rules out the applicability of Vetter and Schultze's treatment.

Thus, relation (1) is not a thermodynamic one and the validity of its application depends on the realization of a number of model assumptions. The

analogy between this relation and the Nernst equation drawn by Vetter and Schultze is therefore doubtful. Relation (1) can however prove useful in the analysis of systems for which the main assumptions of Grahame's model theory are fulfilled to the first approximation[22]. In this case, we can agree with most of the conclusions of Vetter and Schultze[9] regarding the data on the adsorption of ions and molecules at a mercury electrode. Quite rightly, Vetter and Schultze point out that the true value of the partial charge transfer during adsorption (λ in Lorenz's notation) cannot be determined in a purely experimental manner. Their conclusion that Lorenz's coefficients l and $f^{1,2}$ as well as $(x_2-x_1)/x_2$ from Parsons's works have the same physical sense and must coincide, is also correct. It should be noted however that these conclusions were already formulated[3,4].

The greatest objections are raised by Vetter and Schultze's treatment of the adsorption phenomena at platinum metals. Let us dwell on this question in more detail.

Analyzing the adsorption of hydrogen at platinum in electrolyte solutions, Vetter and Schultze do not take into account the fact that this system is not ideally polarized and that in the case of the Pt–H electrode there are two independent components of the system with variable chemical potentials, H_2 and H^+, of which under the condition of necessary electricity supply the double layer can be built*. In connection with this, it is necessary to specify some definitions used earlier in the consideration of an ideal polarized mercury electrode. Namely, in the case of the Pt–H electrode it is not right to identify the Gibbs adsorptions Γ_H and Γ_{H^+} with the quantities A_H and A_{H^-} representing the excess amounts of adsorbed hydrogen and hydrogen ions actually contained in the electric double layer. This question was discussed in detail in ref. 23 and later also in ref. 25. The value of the current flowing during adsorption of ions or uncharged particles on platinum metals is determined by the change of the total, rather than of the free surface charge[23], since it is not only the charge of the metal side of the double layer which changes during adsorption, but also the amounts of adsorbed hydrogen (or oxygen). A method for determination of the adsorption, based on the measurement of the currents arising when adsorbable substances are brought into contact with the electrode under potentiostatic conditions, was proposed in ref. 26.

Vetter and Schultze question the validity of the choice of H and H^+ as the components of the surface layer[23,27]. It should be noted that in refs. 23 and 27 the cases were also considered where the surface layer was built up of H^- and e^- or of H and e^-. As far as thermodynamics are concerned any other pair of particles, *e.g.* H_2 and H_2^+ of H_2 and e^- (*cf.* ref. 25) could equally well be chosen. It is necessary, however, to use a pair of particles since there are two independent components (H_2 and H^+) determining the state of the system, the chemical potential of which can be varied. The relations deduced in refs. 23 and 27 do not depend on the supposed composition of the surface layer, until a nonthermodynamic assumption, justified however by experiment, is introduced. Namely, it is assumed

* In the case of the Hg/Hg_2^{2+} reversible electrode there is only one such component, the chemical potential of the metal remaining constant. If we substitute an amalgam for mercury, that is a metallic phase of variable composition, the thermodynamic treatment of the interfacial layer becomes qualitatively identical with that used in the case of a Pt–H electrode[23,24].

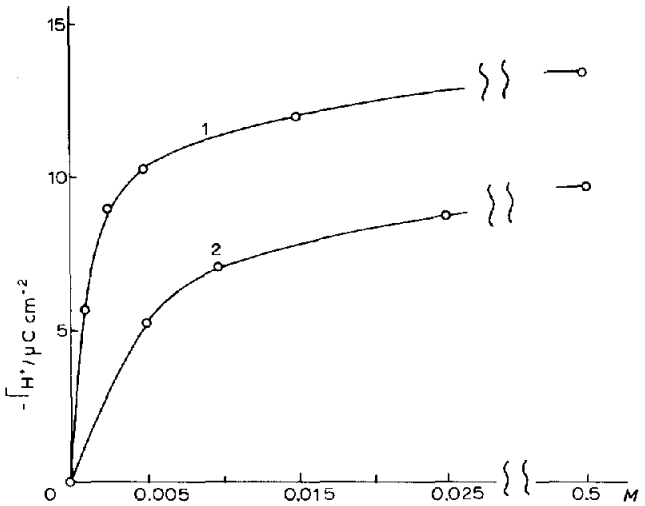

Fig. 1. The dependence of the Gibbs adsorption of hydrogen ions on the cesium (1) and lithium (2) sulfates concentration in 0.005 M H_2SO_4 on a platinized platinum electrode at the reversible hydrogen potential (according to data of ref. 28).

that at sufficiently high concentrations of foreign cations $A_{H^+}=0$ and Γ_{H^+} becomes equal to the free surface charge. This assumption and the choice of the particles H and H^+ as components of the surface layer are supported by the experiments on the displacement of hydrogen ions from the double layer by the solution cations[28,29] (Fig. 1). In a certain range of the neutral salt (Li_2SO_4, Cs_2SO_4) concentrations, added to the initial H_2SO_4 solution, $|\Gamma_{H^+}|$ increases sharply. According to ref. 23:

$$\Gamma_{H^+}=\varepsilon+A_{H^+}$$

At the reversible hydrogen potential ε is negative and A_{H^+} positive. In the absence of foreign cations $A_{H^+}<-\varepsilon$, as a part of the free charge is compensated for by a deficiency of adsorbed anions, and Γ_{H^+} is therefore negative. The observed increase of $-\Gamma_{H^+}$ corresponds to a decrease of A_{H^+}, *i.e.* to the displacement of the hydrogen ions, which were bound by negative surface charges, into the bulk solution. However, when a 3 to 5 fold excess of salt over acid is reached, further increase of salt concentration leads to only a small change of Γ_{H^+}. The amount of adsorbed atomic hydrogen, which can be determined from the charging curve, remains constant within 1–2% over the whole salt concentration range. This experiment shows unambiguously that adsorbed hydrogen ion and hydrogen atom are two different entities.

Vetter and Schultze postulate that in the case of hydrogen ion adsorption on platinum

$$\gamma=A_H/(A_H+A_{H^+}) \tag{9}$$

It is not clear how relation (9) can be obtained from eqn. (1). According to eqn. (9), the value of γ should depend on the presence of foreign electrolyte in solution. In the absence of the supporting electrolyte $\gamma\neq 1$; in particular, in the

"double layer" region in HCl solution $\gamma=0$, since $A_{H^+}=0$ and $A_{H^\cdot}\neq 0$. In the presence of an excess of the supporting electrolyte in the hydrogen region $A_{H^\cdot}=0$ and $\gamma=1$. The use of relation (9) leads Vetter and Schultze to the conclusion that in the case of hydrogen ion adsorption on platinum $\gamma=1$. Apparently, it is the "hydrogen" region which is in question. In this case the assumption that $\gamma=1$ is equivalent to the conclusion about the absence of any polarity of the Pt–H_{ads} bond, which is at variance with experimental data on platinum electrodes.

The problem of the state of adsorbed hydrogen[27,30,31–33] can be solved on the basis of the thermodynamic theory of the hydrogen electrode. The state of H_{ads} can be characterized by the quantity $X=(\partial\varphi/\partial A_H)_{\Gamma_H}$. The calculation of X shows that the bond of adsorbed hydrogen with the electrode surface is of considerable polarity, which depends on potential, metal nature and solution composition, and that H_{ads} affects the electric double layer capacity. In the case of platinum X changes sign with changing surface coverage with H_{ads}, which can be interpreted as the result of formation of two types of hydrogen dipoles, turned with their positive and negative ends, respectively, towards solution. The conclusion about a significant polarity of the Pt–H_{ads} bond is confirmed by experiments on the effect of inorganic anions[31] and Zn^{2+} and Cd^{2+} cations[34,35] on hydrogen adsorption. In the former case a decrease in the bond energy of H_{ads} is observed at small surface coverages with it, whereas in the latter case this energy increases owing to electrostatic interaction between the H_{ads} dipoles turned with their negative ends towards solution and the cations forming part of the electric double layer. These results were obtained under conditions when an excess of foreign salt was present in solution and $A_{H^\cdot}=0$, so that according to relation (9), γ should be equal to 1.

A rigorously thermodynamic interpretation of the charge transfer phenomenon during adsorption at reversible electrodes is given in ref. 6. In accordance with this interpretation, for platinum metals it is possible to introduce two macroscopic coefficients of charge transfer, which characterize the transition of the hydrogen ion H^+_{sol} present in the solution near the electrode surface, into the state of adsorbed atom H_{ads} (coefficient n_1) and the transition of H_{ads} into the state of a free atom H_{sol} near the electrode (coefficient n_2). A thermodynamic relation is valid for n_2 (ref. 6).

$$n_2=\left(\frac{\partial\Gamma_{H^+}}{\partial(\Gamma_H+\Gamma_{H^+})}\right)_{\varphi} \tag{10}$$

Assuming that in solutions with excess of supporting electrolyte $\Gamma_{H^\cdot}+\Gamma_H=A_H$[23], we can write

$$n_2=\left(\frac{\partial\Gamma_{H^+}}{\partial A_H}\right)_{\varphi}=-\frac{X}{Y} \tag{11}$$

where $Y=(\partial\varphi/\partial\Gamma_{H^\cdot})_{A_H}$ is the contribution of the hydrogen ion (or of the double-layer charge) to the potential difference. Since in the presence of a supporting electrolyte excess $\Gamma_{H^+}=\varepsilon$, $\varphi\simeq\psi_u$, and A_H corresponds to the adsorption of H in the compact layer, evidently $-n_2=-(\partial\varepsilon/\partial A_H)_{\psi_u}=\gamma$, *i.e.* it corresponds to the "electrosorption

valency" in the Vetter–Schultze sense for the transition of H_{sol} to H_{ads}. If we proceed from an H_2 molecule rather than from an H atom, this value should be doubled. For determination of n_1 we can use the equation $n_1+n_2=1$, n_1 corresponding to γ for the transition of H^+ to H_{ads}. The calculations show (see ref. 6, Fig. 2) that the value of n_1 can vary from $+0.9$ to $+1.4$ (*i.e.* it differs significantly from unity) and that of n_2 from $+0.1$ to -0.4.

In ref. 6 only one adsorbed state, H_{ads}, is considered. It is not difficult to extend the results[6] to the case when two adsorbed states are taken into account: adsorbed hydrogen ions H^+_{ads} and H_{ads}. This possibility is ensured by the fact that the exchange current of the reaction $H_{ads} \rightleftarrows H^+$ was many times measured in literature[31,36–38]. In this case, in addition to the coefficients considered above, it is necessary to introduce two more macroscopic coefficients of charge transfer which characterize the transition of H^+_{sol} to H^+_{ads} and the transition of H_{sol} to H^+_{ads}. The first of these coefficients is evidently close to zero, because, as shown by the experiments on the displacement of the H^+ ions from the double layer by the supporting electrolyte cations, the H^+ ions have the lowest specific adsorbability on platinum[28,29]. The other coefficient is equal to -1, as the transition from H_{sol} to H^+_{ads} is practically equivalent to the transition $H_{sol} \rightarrow H^+_{sol}$.

The discrepancy between our conclusions and those of Vetter and Schultze, concerning the surface thermodynamics of the Pt–H electrode, must be based on some misunderstanding. Indeed it was shown in ref. 23, p. 92, when discussing the treatment by Plieth and Vetter[5] of Gibbs's relation in the case of reversible electrodes, that "the differences between the relations given by the authors and the formulas given here and partly in our earlier studies are due to different symbols used, while actually their mathematical content is the same".

The interpretation of the Tl^+ ion adsorption on platinum given by Vetter and Schultze[9], does not take into account the Russian works on this problem and is open to objections. The adsorption of Tl^+, especially at potentials close to the hydrogen potential[39], is not a completely reversible process. The measurements at Pt/Pt and smooth electrodes, carried out recently by Kazarinov[40] with the use of the radioactive tracers method, show that only about 10% Tl^+ ions are reversibly adsorbed under these conditions. The adsorption of Tl^+ ions becomes more and more reversible as the potential shifts in the direction of more positive values. Possibly, due to the dependence of the reversibility of the Tl^+ adsorption on potential, the values of γ given by Vetter and Schultze proved to be lower on platinum than on mercury, whereas actually an opposite result should be expected. A more careful verification of the reversibility of the adsorption processes is a necessary prerequisite in calculations also in other cases of adsorption of strongly chemisorbed ions on noble metals, since a significant irreversibility can be observed even in the adsorption of relatively weakly adsorbable zinc ions on Pt and Rh[35,41]*. As shown[42], the Tl^+ adsorption on platinum seems to be accompanied by a transition to the adatomic state in a wide potential range. Otherwise, the adsorption of SO_4^{2-} anions would be expected to occur on the platinum surface

* The widely used potentiodynamic method fails sometimes to disclose the irreversibility of metal cation adsorption on Pt, which becomes apparent when the results of cyclic changes of the cation concentration or of the solution temperature are considered.

covered with adsorbed Tl^+ ions. However, in the presence of Tl^+, in a certain potential range SO_4^{2-} ions are not adsorbed at all, whereas in the presence of Cd^{2+} ions, which seem to retain partly their charge, a considerable adsorption of SO_4^{2-} ions is observed[43].

Finally, it should be remarked that the statement concerning the irreversibility of oxygen adsorption on platinum metals, made in the last section of ref. 9, is not quite exact. In actual fact the oxygen adsorption on Pt, Pd, Rh and Ir at low oxygen coverages is sufficiently reversible to allow the use of the thermodynamic relations for calculation of the contribution of adsorbed oxygen to the potential difference and thus to assess the extent of charge transfer in this process[27,44,45]. The contribution of adsorbed oxygen is greater than that of H_{ads} and the oxygen dipoles are turned with their negative ends towards solution. The conclusion as to the reversibility of the initial stages of the oxygen adsorption on Pt is reached in refs. 46 and 47 as well.

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SUMMARY

A critical analysis shows that the approach to the estimation of the charge transfer in the process of adsorption at the electrode/solution interface used by Vetter and Schultze in the general case is not justified without introduction of non-thermodynamic models. This approach can prove useful in the investigation of the electric double layer within the limits of applicability of Grahame's model. A number of cases can however be cited where the approach of Schultze and Vetter is inapplicable. The conclusions of Schultze and Vetter regarding the adsorption of hydrogen at platinum are apparently based on some misunderstanding. In this case the thermodynamic approach[6,23] should be used.

It would be more correct to call the quantity γ "the formal coefficient of charge transfer", rather than "the electrosorption valency".

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