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DETERMINATION OF FORMAL CHARGE TRANSFER COEFFICIENTS IN ADSORPTION PROCESSES IN THE SYSTEM Hg, Tl, Tl^+, H_2O

I. ELECTROCAPILLARY CURVES OF THE FIRST KIND

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ABSTRACT

The determination of the formal charge transfer coefficient n_2 from the equilibrium electrocapillary curves of the first kind (taken under the condition μ_{Tl^+} = const) leads to values which are close to the values of the quantity l of Lorenz, obtained from a.c. measurements.

The discussion of the charge state of adsorbed particles in chemisorption processes [1—15] has shown that at present there exist different approaches to the problem of charge transfer through the interface, which are associated with different definitions of the latter. The choice of the interface according to Gibbs, i.e. its localization in the region where the adsorption, say, of the solvent is taken to be zero, allows the Gibbs adsorption of the oxidized and reduced forms Γ_O and Γ_R of a redox system to be determined experimentally and the calculation for this system of the formal charge transfer coefficients n_1 and n_2 [7,10,11,15], described for a two-step reaction of the type

$$O + n_1e \rightleftharpoons A \qquad (a)$$

$$A + n_2e \rightleftharpoons R \qquad (b)$$

(A is the intermediate adsorbed state of the substance) by the equations

$$n_1 = (\partial \Gamma_R/\partial \Gamma_\Sigma)_\varphi \qquad (1)$$

and

$$n_2 = (\partial \Gamma_O/\partial \Gamma_\Sigma)_\varphi \qquad (2)$$

where $\Gamma_\Sigma = \Gamma_O + \Gamma_R$ and $n_1 + n_2 = 1$, or in the case under consideration in this communication

$$n_1 = (\partial \Gamma_{Tl}/\partial \Gamma_\Sigma)_\varphi \qquad (1a)$$

$$n_2 = (\partial\Gamma_{Tl^+}/\partial\Gamma_\Sigma)_\varphi \tag{2a}$$

and $\Gamma_\Sigma = \Gamma_{Tl} + \Gamma_{Tl^+}$. The localization of the interface is determined by the condition $\Gamma_{Hg} = 0$, the chemical potentials of H_2O, K^+ and NO_3^- are assumed to be approximately constant [17].

The definition of the interface in the microphysical sense according to Lorenz [13] as a real boundary between metal and solution leads to the description of charge transfer by the value of the elementary or true charge transfer coefficient λ, characterizing the portion of the charge transferred through such interface, and of the experimentally determinable coefficient

$$n \approx l = \lambda \pm (\partial\epsilon/\partial\Gamma_\Sigma)_\varphi$$

taking account of the influence of adsorption on the electrode charge, where ϵ is the true (free) electrode charge. In the case when adsorbed particles do not affect the distribution of the double layer charges, the quantities n, corrected for different localizations of the interface, are identical with λ. But if $(\partial\epsilon/\partial\Gamma_\Sigma)_\varphi \neq 0$, n is close to l [15]. In fact, the coefficient l is determined from the relation

$$C^*(0) = zFl\,\partial\Gamma_\Sigma/\partial\varphi$$

$$C^*(0) = C_p(0) - C_p(\infty) \approx C(0) - C_D$$

$C_p(0)$, $C_p(\infty)$ are the capacities calculated for a parallel circuit at $\omega \to 0$ and $\omega \to \infty$ respectively, and C_D is the capacity of the supporting electrolyte solution [13]. Thus,

$$zFl\,\Gamma_\Sigma \approx \int C(0)\,d\varphi - \int C_D\,d\varphi + \text{const} = Q - \epsilon_0 + \text{const} \tag{3}$$

where Q is the total charge in the system under consideration and ϵ_0 is the free charge in the supporting electrolyte solution.

If we assume, as Lorenz does, that const in eqn. (3) does not depend on Γ_Σ,

$$zFl \approx \partial Q/\partial\Gamma_\Sigma$$

but according to ref. 16

$$n_2 = \partial\Gamma_O/\partial\Gamma_\Sigma = (1/zF)\,\partial Q/\partial\Gamma_\Sigma$$

whence $l \approx n$.

Thus, Lorenz's coefficient l can be determined not only from impedance measurements, but also from thermodynamic data as was already indicated by Parsons [20]. In this communication the values of n_2 have been calculated from the data on the Gibbs adsorption of thallium in the system Tl/Tl^+, obtained by us in refs. 17 and 18 in the measurement of the σ, φ dependence by means of the equilibrium electrocapillary (EC) curves (Fig. 1) *.

* In this and the next figures the potentials are referred to an amalgam reference electrode of composition 9.9 at.% Tl (Hg) in 0.1 M $TlNO_3$ + 0.9 M KNO_3 solution.

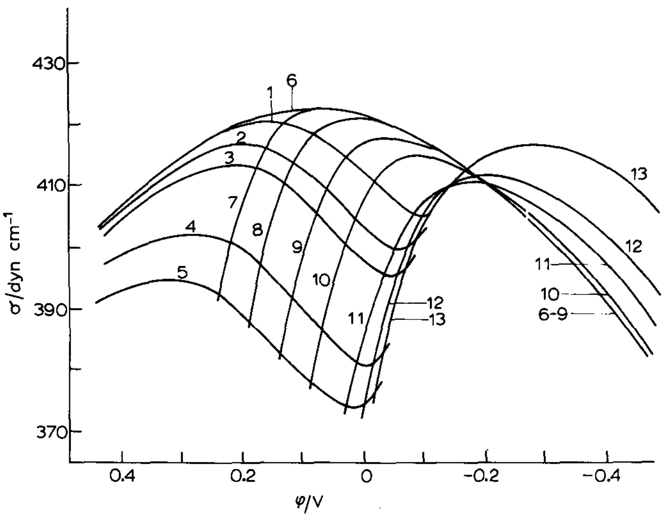

Fig. 1. EC curves of the 1st and 2nd kind plotted together. Tl^+ concentration in x M $TlNO_3$ + $(1-x)$ M KNO_3: (1) 0.001, (2) 0.005, (3) 0.01, (4) 0.05, (5) 0.1 (EC curves of the 1st kind). Tl content in amalgams in at.%: (6) 0, (7) 0.002, (8) 0.014, (9) 0.12, (10) 0.7, (11) 4.9, (12) 7.8, (13) 20.7 (EC curves of the 2nd kind).

Figures 2 and 3 show the dependences of Γ_{Tl^+} and Γ_Σ on φ, necessary for calculation of n_2, which have been calculated along the EC curves of the first kind by the formulas

$$\Gamma_\Sigma = -(\partial\sigma/\partial\mu_{Tl^+})_\varphi \tag{4}$$

and

$$\Gamma_{Tl^+} = \Gamma_\Sigma - \Gamma_{Tl} \tag{5}$$

where

$$\Gamma_{Tl} = (\partial\sigma/\partial\varphi)_{\mu_{Tl^+}}$$

and along the EC curves of the second kind in the manner described in the next communication.

Γ_Σ at the intersection points of the EC curves of the 1st and 2nd kind can be calculated also by the formula

$$\Gamma_\Sigma = (\partial\sigma/\partial\varphi)_{\mu_{Tl^+}} - (\partial\sigma/\partial\varphi)_{\mu_{Tl}}$$

as was done in refs. 17 and 18. A graphical differentiation of the dependences of Γ_{Tl^+} on Γ_Σ, plotted from the data of Figs. 2 and 3 for several values of φ = const, at the points corresponding to a certain chosen constant concentration of thallium ions, gives according to (2a) the values of n_2 for φ = const at this concentration. In this case, n_2 in the range φ = 0.4—0.05 V, calculated from the Γ_{Tl^+}, Γ_Σ dependences for the EC curves of the 1st kind give $(\partial\Gamma_{Tl^+}/\partial\Gamma_\Sigma)_\varphi$ at μ_{Tl^+} = const. Figure 4 shows the dependences of n_2 on φ, obtained at c_{Tl^+} =

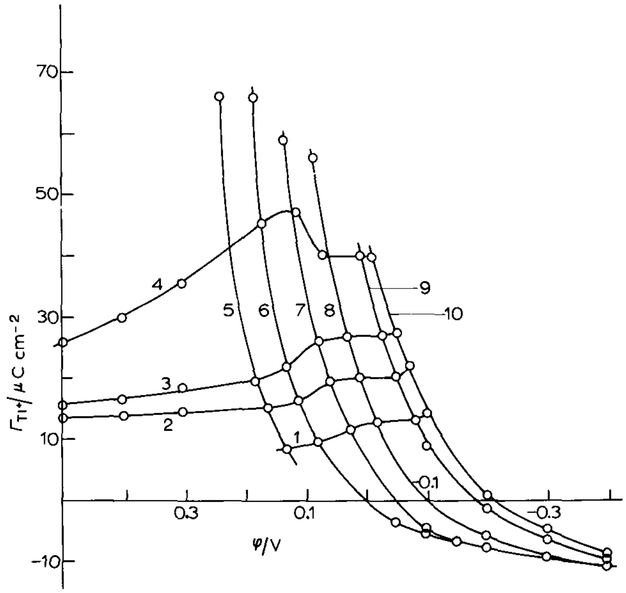

Fig. 2. Γ_{Tl^+}, φ dependence along the EC curves of the 1st and 2nd kind, calculated from the EC curves satisfying the conditions: (1) 0.001, (2) 0.005, (3) 0.01, (4) 0.05 *M* Tl^+; (5) 0.002, (6) 0.014, (7) 0.12, (8) 0.7, (9) 4.9, (10) 7.8 at.% Tl.

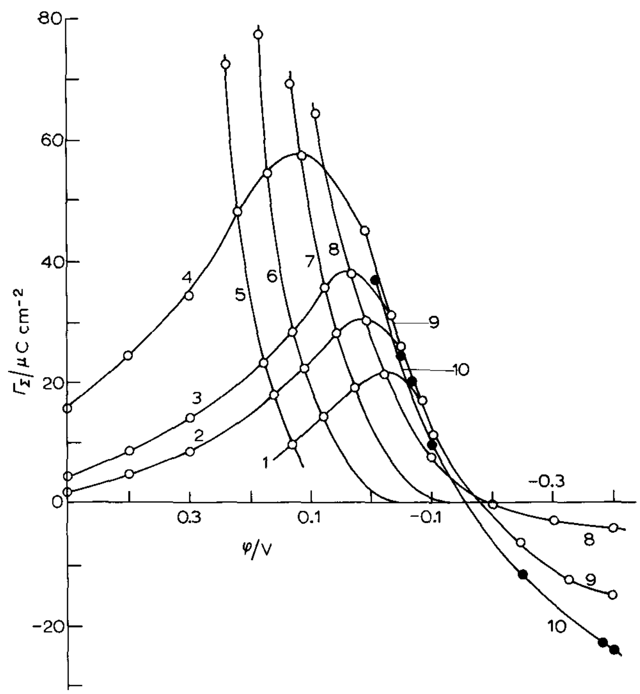

Fig. 3. Γ_{Σ}, φ dependence along the same EC curves as in Fig. 2.

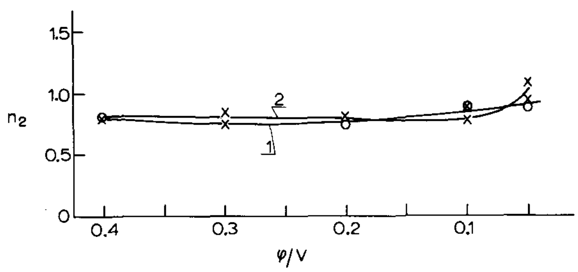

Fig. 4. Dependence of n_2 on φ, calculated by means of (○) eqn. (2a) and (x) eqn. (6) from the data of the EC curves of the 1st kind. c_{Tl^+} : (1) 0.01 M, (2) 0.04 M.

0.01 and 0.04 M, where the n_2 values, calculated by (2a) are designated by circles. Since the quantities Γ_{Tl^+} and Γ_Σ are functions of φ and μ_{Tl^+} (or φ and μ_{Tl}), the values of n_2 can be obtained also from the relation

$$n_2 = (\partial\Gamma_{Tl^+}/\partial\mu_{Tl})_\varphi/(\partial\Gamma_\Sigma/\partial\mu_{Tl^+})_\varphi \quad (6)$$

from the curves of the 1st kind. In this case, in order to obtain the dependences of n_2 on φ in the potential range corresponding to the curves of the 1st kind, the dependences of Γ_{Tl^+} on μ_{Tl^+} and of Γ_Σ on μ_{Tl^+} are graphically differentiated for several φ = const in the range 0.4—0.05 V at the points corresponding to the chosen concentration of Tl^+ ions (c_{Tl^+} = const). The values of n_2 calculated by means of eqn. (6) in Fig. 4 are designated by crosses. As is clear from Fig. 4, the results of calculations by both methods show good agreement.

The graphical differentiation of the dependences of Γ_{Tl^+} on Γ_Σ (or Γ_{Tl} on Γ_Σ) for φ = const at the points corresponding to some chosen constant Γ_Σ gives the values of n_2 (n_1 respectively) for some values of φ at Γ_Σ = const. It can be seen from Table 1 listing the values of n_1 and n_2 calculated by means of (1a) and (2a) for Γ_Σ = 10, 20 and 30 μC cm^{-2} plotted along the EC curves of the 1st kind, that the sum of n_1 and n_2 for different φ is really close to 1, which confirms the correctness of calculations.

As is clear from Fig. 4 and the Table, at sufficiently positive φ, corresponding to the region of Lorenz's impedance and pulse measurements, the values of n_2, calculated at Γ_Σ = const and also at c_{Tl^+} = const, agree well with Lorenz's

TABLE 1

φ/V	$\Gamma_\Sigma = 10$			$\Gamma_\Sigma = 20$			$\Gamma_\Sigma = 30$		
	n_1	n_2	$n_1 + n_2$	n_1	n_2	$n_1 + n_2$	n_1	n_2	$n_1 + n_2$
0.4	0.20	0.82	1.02	0.15	0.82	0.97			
0.2				0.25	0.75	1.0	0.19	0.80	0.99
0.1				0.29	0.73	1.02	0.17	0.80	0.97
0.05				0.32	0.73	1.05			

value of l_1 = 0.6—0.8 [13,19]. The quantity designated by Lorenz as l_1, corresponds namely to process (b), that is to our n_2.

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