THE VOLTA POTENTIAL AT AN ELECTRODE – SOLUTION INTERFACE AT THE ZERO-CHARGE POTENTIAL

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The process of equalization of electrochemical potentials in the establishment of electrochemical equilibrium involves both directed migration of ions through the metal–solution boundary and flow of free electrostatic charges, which create the electric field in the gas phase, from the surface of one phase to the other [1, 2]. The latter process is often ignored (see, for example, [3, 4]), leading to the conclusion that the Volta potential is zero at an electrode–solution interface at the zero-charge potential, irrespective of the natures of the metal and solvent [5-7]. The erroneousness of this conclusion is demonstrated by the experimental result of Randles [8], who found that $(\Delta_{H_2O}\psi)_{q=0} = -0.26$ V. Adsorption of water vapor on the surface of freely dropping mercury can in principle alter the work function W_e^{Hg} and thus cause an error in the experimental value of $(\Delta^{Hg}_{H_2O}\psi)_{q=0}$. However, since the presence of water vapor has practically no influence on W_e^{Hg} over a wide range of pressures [9], we can suppose that this error is very small, and that the value found by Randles for $(\Delta^{Hg}_{H_2O}\psi)_{q=0}$ is correct.

In this article we attempt to determine the quantity $(\Delta^{M}_{L}\psi)_{q=0}$ for a number of other systems, where the solvent L can be not only water but methanol, ethanol, acetone, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO), and the metals are mercury and bismuth.

From Fig. 1 it follows that the difference between the zero-charge potentials of the same metal M in water and in a solvent L, including the potential difference at the interface between the liquids, is

$$(\Delta E_{q=0})_M = E^{L}_{q=0} - E^{H_2O}_{q=0} = -(\Delta^{M}_{H_2O}\psi)_{q=0} + \Delta^{L}_{H_2O}\psi + (\Delta_L{}^{M}\psi)_{q=0}, \quad (1)$$

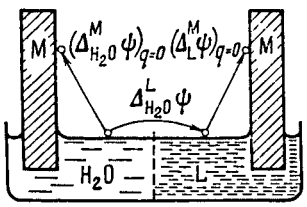

Fig. 1

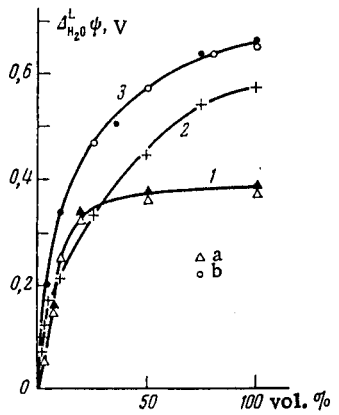

Fig. 2

Fig. 1. Schematic diagram of circuit consisting of two identical metals at the zero-charge potential in water and a nonaqueous solvent L.

Fig. 2. Graphs of Volta potential $\Delta^{L}_{H_2O}\psi$ vs volumetric contents of ethyl alcohol (1), dimethyl sulfoxide (2), and dimethylformamide (3). a) Data from [19]; b) from [20].

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TABLE 1. Differences of Zero-Charge Potentials and Volta Potentials at Interface between Solutions

System	$(\Delta E_{q=0})_{Hg}$, V	$(\Delta E_{q=0})_{Bi}$, V	$\Delta^{L}_{H_2O}\Psi$, V
Water–methanol	0,13 [10, 11]	0,14 [15]	0,38 [19]
Water–ethanol	0,20 [10]	0,20 [16]	0,37
Water–DMF	0,24 [12]	0,25 [17]	0,65
Water–DMSO	0,15 [13]	0,15 [18]	0,57
Water–acetone	0,22 [14]	–	0,57

TABLE 2. Volta Potentials at Mercury–Solution and Bismuth–Solution Interfaces at the Zero-Charge Potential of the Metal

Solvent	$(\Delta^{M}_{L}\psi)_{q=0}$, V		Solvent	$(\Delta^{M}_{L}\psi)_{q=0}$, V	
	for Hg	for Bi		for Hg	for Bi
Water	−0,26 *	−0,24	DMF	−0,67	−0,64
Methanol	−0,51	−0,48	DMSO	−0,68	−0,66
Ethanol	−0,44	−0,42	Acetone	−0,61	–

* Data from [8].

where $\Delta^{L}_{H_2O}\psi$ is the Volta potential at the interface between the two liquids. Table 1 lists values of $(\Delta E_{q=0})_{Hg}$ and $(\Delta E_{q=0})_{B}$ for the above solvents on the basis of the experimental data in [10-18].

The Volta potentials $\Delta^{L}_{H_2O}\psi$ for the systems water–methanol and water–ethanol were determined by Frumkin [19], and those for the system water–DMF by Ganzhina et al. [20]. In both cases $\Delta^{L}_{H_2O}\psi$ was found by the vertical-jet method of Kenrick [1], which requires a considerable expenditure of the solvents. In order to reduce the consumption of solvents, we measured the Volta potentials $\Delta^{L}_{H_2O}\psi$ by the horizontal-jet method suggested by Gerovich and Frumkin [21].

The principle of this method is as follows: a standard solution (0.05 N KCl in water) emerges as a jet from a horizontal capillary and separates into drops above a central funnel containing the test solution. The jet flows 2-3 mm above the funnel at 12-14 ml/min, and the drops from the disintegrating jet do not fall on the surface of the test solution in the funnel. By means of salt bridges (with saturated KCl solution in water), the jet and the test solution are connected to calomel electrodes; the potential difference between the latter, E, is measured by a potentiometer with a high-resistance null-instrument ($R \geq 10^{12}\ \Omega$). The voltage E was measured twice: first when aqueous solution was present in the funnel, and then when it was replaced by nonaqueous solution. As one can easily verify, the difference ΔE gives the Volta potential $\Delta^{L}_{H_2O}\psi$.

We studied the following solutions: 0.01 N KCl in ethanol; 0.1 N $NaClO_4$ in DMF and DMSO; 0.1 N LiCl in acetone; and the corresponding solutions in water–ethanol, water–DMF, and water–DMSO mixtures. We plotted $\Delta^{L}_{H_2O}\psi$ vs the volumetric proportions of ethanol, DMF, and DMSO (Fig. 2). The same figure plots literature data [19, 20] for water–ethanol and water–DMF mixtures, obtained by Kenrick's vertical-jet method. As we see from Fig. 2, there is good agreement between the different methods of determining $\Delta^{L}_{H_2O}\psi$. The values of $\Delta^{L}_{H_2O}\psi$ corresponding to the transition from water to the pure nonaqueous solvent are listed in Table 1.

From Table 1 by means of Eq. (1) we determined the values of $(\Delta^{Hg}_{L}\psi)_{q=0}$ on the assumption that $(\Delta^{L}_{H_2O}\psi)_{q=0} = -0.26$ V [8]. The results are listed in Table 2.*

To determine the corresponding Volta potentials for bismuth, it was necessary to find the value of

*The slight discrepancy with the results $(\Delta^{Hg}_{CH_3OH}\psi)_{q=0} = -0.53$ V and $(\Delta^{Hg}_{DMF}\psi)_{q=0} = -0.63$ V given in [2] is due to a disagreement between the original data for $\Delta^{L}_{H_2O}\psi$, and also to the fact that in calculating $(\Delta^{Hg}_{DMF}\psi)_{q=0}$, Frumkin et al. [2] did not allow for specific adsorption of ClO_4^- ions at the Hg–water interface, which causes $E_{q=0}$ to shift toward the negative by about 0.03 V.

$(\Delta^{Bi}_{H_2O}\psi)_{q=0}$. For this prupose we used the following general equation [2]:

$$E^{M_2}_{q=0} - E^{M_1}_{q=0} = [W_e^{M_2}/F + (\Delta_L^{M_2}\psi)_{q=0}] - [W_e^{M_1}/F + (\Delta_L^{M_1}\psi)_{q=0}], \quad (2)$$

relating the difference of zero-charge potentials of two metals in the same solvent to their work functions and the corresponding Volta potentials at the metal–solution interface. Since in aqueous solutions of fluorides $E^{Bi}_{q=0} - E^{Hg}_{q=0} = -0.19$ V [1, 18], and since according to Trasatti [22] the most reliable value of $(W^{Bi}_e - W^{Hg}_e)/F$ is -0.21 V, from Eq. (2) we find that $(\Delta^{Bi}_{H_2O}\psi)_{q=0} = (\Delta^{Hg}_{H_2O}\psi)_{q=0} + 0.02 = -0.24$ V. Then, using the data in Table 1, we can find the values of $(\Delta^{Bi}_{L}\psi)_{q=0}$ for methanol, ethanol, DMF, and DMSO (Table 2).

As we see from Table 2, for all the systems in question the Volta potential $(\Delta^{M}_{L}\psi)_{q=0}$ differs appreciably from zero, and depends markedly on the nature of the solvent. Thus calculations of the "theoretical zero points" based on the assumption that $(\Delta^{M}_{L}\psi)_{q=0} = 0$ [4-7] have no basis in fact, and can only lead to erroneous conclusions. The relation between the zero-charge potentials and the work functions has recently been discussed in more detail by Frumkin et al. [2] and Trasatti [22].

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