POTENTIAL DIFFERENCE AT THE BOUNDARY BETWEEN DILUTE SOLUTIONS OF ELECTROLYTES AND AIR

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The published data on the dependence of the surface potential at the solution/air boundary on the concentration of the electrolyte in the region of dilute solutions are contradictory.

According to the data of Gerovich [1], small potential shifts toward the positive side were observed on passing from 0.01 N potassium chloride to more dilute solutions of electrolytes (10^{-6} to 10^{-3} N), and the potential of "pure" water were found to be approximately 24 mV more positive than the surface potential of 0.01 N potassium chloride. With increase in the concentration of the electrolyte or with addition of multiply charged cations the positive potential of water disappeared. The electrolyte concentration at which the disappearance of the potential was observed depended on the nature of the cation. Klein and Lange [2] found that the surface potential of the solution does not change in the region of concentrations from $7 \cdot 10^{-7}$ to 10^{-1} N. Buhl [3], when measuring the potentials of solutions with concentrations from 10^{-4} to 10^{-1} N by the vertical-stream method of Kenrick, found that the adsorption potential difference at the water/air boundary was 5.5 mV. In the work by Exerowa [4], devoted to investigation of the effect of the adsorption of surface-active substances and the composition of the solution on the potential of the diffuse electrical layer (φ_0) at the solution/air boundary, φ_0 was obtained from the dependence of the thickness of the equilibrium liquid film on the applied pressure [5]. For dilute solutions of potassium chloride (10^{-5} N) in the absence of surface-active substances φ_0 was found to be equal to 27 mV; the value of φ_0 increased further with further dilution and depended on the pH.

In connection with these data we again turned our attention to investigation of the dependence of the surface potentials in dilute solutions of potassium chloride on the concentration. We paid particular attention to the purification of the reagents and the water.

The adsorption potential difference ($\Delta\chi$) was measured by the radioactive probe method [6] in the form described in [7]. In this variant the source of α radiation is separate from the measurement electrode (a small gold gauze). An electrometric U1-2 direct-current amplifier was used as recording instrument. The quantity $\Delta\chi$ was determined as the difference between the measured emfs of two cells: 1) sat.c.e./sat.KCl/10^{-2} N KCl/air/probe; 2) sat.c.e./sat.KCl/investigated solution/air/probe. The experimental $\Delta\chi$ values were corrected for the value of the diffusion potential at the xN KCl/10^{-2} N KCl boundary (x from 10^{-5} to 10^{-3}), calculated by means of the Henderson formula [8], on the assumption that the mobilities of the K^+ cation and Cl^- anion are 64.5 and 65.3 respectively (at 18°C). The correction did not exceed 1 mV.

In spite of the small spread of the data, the measurements showed that for dilute solutions the adsorption potential difference at the solution/air boundary does not in any case exceed 5-6 mV, which is close to the results obtained by Buhl [3], and within the limits of 2-3 mV does not depend on the electrolyte concentration in the range of concentrations between 10^{-3} and 10^{-5} N. Similar results were obtained in dilute solutions of potassium iodide and potassium hydroxide. Within the indicated concentration limits no dependence on the pH of the solution was observed.

The reason for the discrepancy with Exerowa's conclusions remains unclear. It must be supposed that the potential differences arising at the surface of the thin film differ significantly from the potential difference at the free surface of water with normal geometrical dimensions. The discrepancy could also be

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explained on the supposition of an irregular variation of potential as a function of the distance from the interface. In this case the overall effect could be measured in our experiments, and only part of it in Exerowa's experiment. It is, however, difficult to explain the different dependence on the pII of the solution on the basis of such a scheme.

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