HIGH VOLTA POTENTIALS AT HEPTANE – WATER INTERFACE IN PRESENCE OF VALINOMYCIN

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We showed in a previous paper that the potentials at a heptane–water interface when a transmembrane potential is induced in the presence of the cyclic antibiotic valinomycin (VM) are nonadditive [1]. It was of interest to use different methods to investigate the relationship between the potential difference at a heptane–water boundary and the K^+ ion concentration in a cell containing only a single water-nonwater boundary. The cells used can be represented as follows:

$$\begin{array}{ccccccccccc} & 1 & & 2 & & 3 & & 4 & & 5 & & 6 & \\ \text{Au} & | & \text{air} & & | & \text{heptane} & | & \text{KCl, VM (water)} & | & \text{KCl}^{\text{sat}}\ \text{(water)} & | & \text{Hg}_2\text{Cl}_2 & | \ \text{Hg} \\ & & \varphi_{12} & & & \varphi_{23} & & \varphi_{34} & & \varphi_{45} & & \varphi_{56} & \end{array} \qquad (1)$$

$$\begin{array}{ccccccccccc} & 1 & & 3 & & 4 & & 5 & & 6 & & & \\ \text{Au} & | & \text{heptane} & & | & \text{KCl, VM (water)} & | & \text{KCl}^{\text{sat}}\ \text{(water)} & | & \text{Hg}_2\text{Cl}_2 & | & \text{Hg} & \\ & & \varphi_{13} & & & \varphi_{34} & & \varphi_{45} & & \varphi_{56} & & & \end{array} \qquad (1a)$$

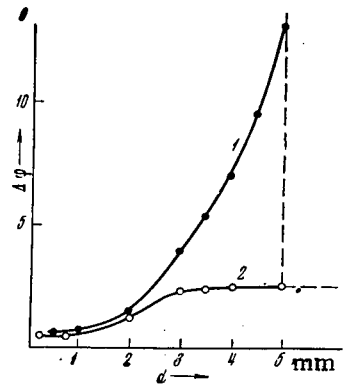

Fig. 1

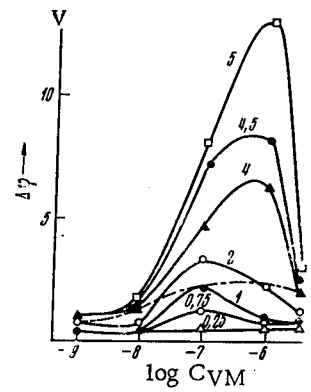

Fig. 2

Fig. 1. Potential in heptane–water system measured by vibrating capacitor method as function of thickness of heptane layer at amplitudes of: 1) 1 mm; 2) 0.1 mm. The broken line is for cell (1), d > 5 mm; the continuous lines are for cell (1a).

Fig. 2. Volta potential measured by vibrating capacitor method for different thicknesses of heptane layer as function of VM concentration in cell (1a) (thickness given in mm). The broken line is the same relationship for cell (1).

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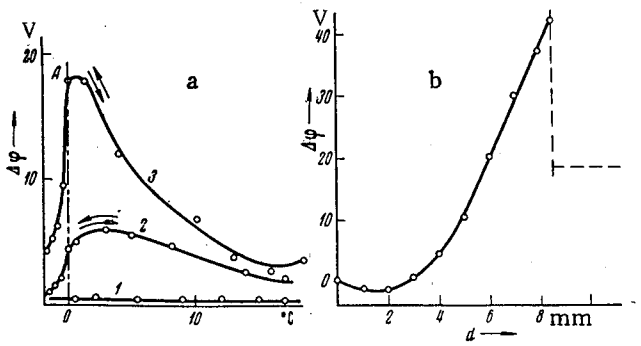

Fig. 3. a) Volta potential in cell (1) as function of temperature: 1) 10^{-2} M KCl; 2) 10^{-2} M KCl + 10^{-7} M VM; 3) 10^{-2} M KCl + 10^{-6} M VM; b) potential as function of depth of submersion of vibrating electrode in heptane phase (0°, 10^{-2} M KCl + 10^{-6} M VM) (continuous line), and Volta potential obtained for cell (1) at point A in Fig. 3a (broken line).

In the case of cell (1) the measurements were made with a vibrating capacitor and a radioactive plutonium probe with activity 0.075 μCi, which ionized the space between the gold grid and the aqueous phase. In the case of cell (1a) the gold electrode was directly immersed in the heptane phase and the measurements could be made with different vibration amplitudes and different thicknesses d of the heptane layer between the reference electrode and the aqueous phase. Otherwise the measurements and preparation of the solutions were the same as in [1]. All the potentials on the plots are relative to the gold reference electrode. Figure 1 shows the results of one of the experiments for cells (1) and (1a) containing 10^{-2} M KCl and 10^{-6} M VM and aqueous phase 4, with which the heptane was first brought into equilibrium, for maximum (curve 1) and minimum (curve 2) vibration amplitudes of the reference electrode. When the reference electrode vibrated in air [cell (1), d > 5 mm], the measured Volta potential did not depend on the vibration amplitude. When the electrode was immersed in heptane [cell (1a)], the result of measurement depended on the vibration amplitude until the amplitude became less than 0.1 mm. At this minimum amplitude the results of measurements of the Volta potential for cell (1) and cell (1a) close to the free heptane surface were similar. At maximum vibration amplitude the measured potential increased with increase in d without any sign of leveling off and attained 13 V close to the heptane surface in this experiment. Fluctuations in the activity of different batches of VM, which were reported in [1], at high amplitudes were greatest close to the heptane surface. When the gold electrode was submerged deeply in the heptane layer the differences decreased.

Figure 2 shows the results of potential measurements in cell (1a) and (1) (broken line) with different VM concentrations in the system. The measurements with cell (1a) were made with the vibrating electrode at different depths and at maximum vibration amplitude. The highest potentials were obtained with a VM concentration of $10^{-7} - 10^{-6}$ M and with the vibrating electrodes at maximum distance from the heptane–water boundary. In the presence of VM high Volta potentials arise in a heptane–water system when it cools even without insertion of the vibrating electrode into the heptane. Figure 3a, curve 1, shows that the Volta potential in cell (1) was independent of the temperature in the case of a system without antibiotic. The presence of even 10^{-7} M VM (Fig. 3a, curve 2), however, led to a considerable variation of the potential with temperature. At 10^{-6} M VM (Fig. 3a, curve 3) the effect in cell (1) at a temperature close to zero reached 18 V. When the reference electrode was immersed in heptane and vibrated at maximum amplitude the observed effect was 40 V when the heptane layer was 8 mm thick (Fig. 3b). We investigated contact effects in systems (1) and (1a) with different KCl content more fully by comparing the results obtained by the vibrating capacitor method and the radioactive probe method (Fig. 4). As Fig. 4 indicates, the plots of Volta potential in cell (1) against C_{KCl} are nonmonotonic in either case. The effects measured by the radioactive probe method, however, lie in the range of hundreds of millivolts, whereas the vibrating capacitor method gives values measured in volts. When the reference electrode was immersed in heptane the potentials registered by both methods

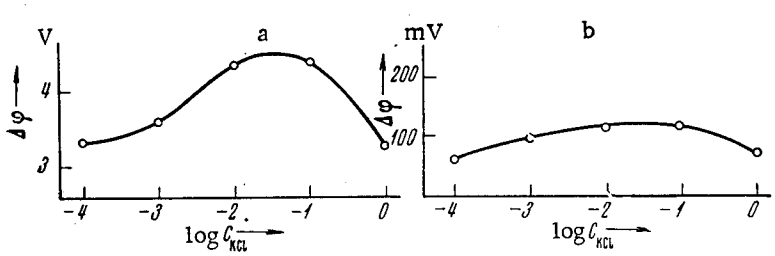

Fig. 4. Potential as function of potassium ion concentration in Cell I (10^{-7} M VM): a) by vibrating capacitor method; b) by radioactive probe method.

became comparable when the thickness of the heptane layer was reduced. It should be borne in mind that Volta potentials measured by the different methods on a water–air interface usually agree fairly well with one another [2]. According to published data, a hydrocarbon–water system behaves in a similar way. If the hydrocarbon is a good dielectric, an adsorption potential is observed [3].

The results obtained in the present investigation indicate the presence of two effects. The first effect, observed at low amplitudes in cell (1a), characterizes the spontaneous charging of heptane in equilibrium with the aqueous phase in the presence of VM. If the vibration amplitude is small, a difference between the potentials in cell (1) and (1a) means that $\varphi_{12} + \varphi_{23}$ is not equal to φ_{13}. Reduction of temperature leads to an increase in the spontaneous charging of heptane and to unusually high potentials. This effect is reversible until the aqueous part of the system freezes (Fig. 3a).

If the number of mobile charges in heptane is artificially increased, which occurs when the radioactive probe is used, high Volta potentials are not observed (Fig. 4). An increase in the number of mobile charges can also account for the reduction of the effect when the VM content of the system is high (Fig. 2). In this case charged structures, including ions (KVM^+), water molecules, and possibly certain counterions accumulate in the heptane. The nature of the particles responsible for the charging of the heptane, however, is still not clear. Unipolar charging of the heptane phase proceeds until the electric field produced prevents further penetration of charges into the heptane.

If the vibration amplitude is small the heptane phase containing the space charge exhibits another property, viz., additional electrification of the heptane layer, which depends on the vibration amplitude of the reference electrode when it is situated far from the aqueous phase (Fig. 1, curves 1 and 2; Fig. 3). This second effect also depends on the composition of the cell (Fig. 2). The potential registered in the second case can also be observed in a completely symmetric Au(heptane)Au system, if the heptane layer is first brought into equilibrium with the aqueous phase of cell (1). Such effects are not observed in this system if pure heptane is used. Manifestation of the second effect, which is probably due to electrokinetic phenomena, requires not only the presence of valinomycin, but also a vibration amplitude of the vibrating capacitor in excess of a certain limit.

LITERATURE CITED

1. A. N. Frumkin, M. I. Gugeshashvili, and L. I. Boguslavskii, Dokl. Akad. Nauk SSSR, 198, 1452 (1971).
2. A. N. Frumkin, Tr. Fiz.-Khimich. Inst. im L. Ya. Karpova, No. 4, 75 (1924).
3. J. T. Davies and E. K. Rideal, Interfacial Phenomena, New York (1961), p. 66.