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Figure 1: Fig. 1. Differential-capacitance curves at 750 cps in 0.01 N solutions: 1 –(N(C4H9)4)Br, 2 –(N(C2H5)4)Br, 3 –(N(CH3)4)Br, 4 –KBr

## Abstract

## Full Text

## PHYSICAL CHEMISTRY

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# EFFECT OF TETRAALKYLAMMONIUM SALTS ON THE CAPACITANCE OF THE DOUBLE LAYER IN SOLUTIONS OF BUTYL ALCOHOL

*(Presented by Academician A. N. Frumkin, 17 VI 1960)*

The effect of tetraalkylammonium salts on electrode processes was studied in the works of Frumkin and co-workers [1–3]. The results obtained were explained by the considerable adsorption of these organic cations on the mercury electrode.

It was of interest to study the combined effect on the differential capacitance of the adsorption of neutral organic molecules and surface-active organic cations. To this end we investigated the effect of potassium bromide and tetraalkylammonium salts on the capacitance of the double layer in the presence of butyl alcohol.

The investigation was carried out on a dropping mercury electrode by the impedance-bridge method described in [4–7]. The frequency of the alternating current was 750 cps. The measurements were made at room temperature. A normal calomel aqueous electrode (n.c.e.) served as the reference electrode.

The salts used by us were recrystallized three times from bidistillate. KBr was ignited, while $(N(CH_3)_4)Br$ and $(N(C_2H_5)_4)Br$ were dried at 100–120°, and the preparations obtained in this way gave coincident results. The differential capacitance was measured in electrolyte solutions at concentrations of 1; 0.1, and 0.01 $N$; the concentration of butyl alcohol was varied from $5.5 \cdot 10^{-4} M$ to $5.5 \cdot 10^{-1} M$; the butyl alcohol was purified by the method of Lund and Bjerrum [8].

**Fig. 1.** Differential-capacitance curves at 750 cps in 0.01 $N$ solutions: 1 –$(N(C_4H_9)_4)Br$, 2 –$(N(C_2H_5)_4)Br$, 3 –$(N(CH_3)_4)Br$, 4 –KBr.

The curves $C$–$\varphi$, obtained on the dropping electrode in aqueous solutions, are

Figure 2

Figure 2: Figure 2

shown in Fig. 1. The magnitude of the capacitance at negative polarizations depends on the background cations and decreases in the series

$$K^+ > (N(CH_3)_4)^+ > (N(C_2H_5)_4)^+ > (N(C_4H_9)_4)^+$$

as a result of the increase in the cation radius and the decrease in the effective dielectric constant in the double electri-

layer. As can be seen from Fig. 1, on the $C-\varphi$ curves measured in solutions of $(N(CH_3)_4)Br$ and $(N(C_2H_5)_4)Br$ at small positive surface charges, there is a small "hump," characteristic of aqueous solutions of inorganic salts ([9]), and the magnitude of the capacitance in this part of the curve increases on going from $K^+$ to $(N(C_2H_5)_4)^+$. This phenomenon is associated with the fact that specific adsorption of the cation leads to an increase in the number of $Br^-$ anions in the double layer and, consequently, to an increase in the differential capacitance.

**Fig. 2.** Differential-capacitance curves at 750 Hz in solutions:
1–0.01 $N$ KBr + $5.5 \cdot 10^{-2}$ $M$ $C_4H_9OH$,
2–0.1 $N$ KBr + $5.5 \cdot 10^{-2}$ $M$ $C_4H_9OH$,
3–0.01 $N$ KBr, 4–0.1 $N$ KBr.

Increasing the concentration of the background electrolyte leads to an increase in capacitance on the positive branch of the $C-\varphi$ curve, while the shape of the curve changes only slightly.

In the case of KBr, when the concentration is increased, the "hump" on the curve is retained, and the capacitance in this part of the curve increases as a result of increased adsorption of the $Br^-$ anion. At the same time, in the case of $(N(C_2H_5)_4)Br$ (and also $(N(CH_3)_4)Br$), when the concentration is increased –for example, on going from a 0.01 $N$ to a 0.1 $N$ solution–a bend appears on the capacitance curve instead of the "hump."

This phenomenon is apparently associated with a strong increase in the adsorption of $Br^-$ under the influence of specifically adsorbing organic cations.

An increase in the concentration of the background also affects the cathodic branch of the $C-\varphi$ curve. In the case of KBr, increasing the concentration leads to a shift of the minimum toward negative potentials and to an increase in capacitance over the entire cathodic branch of the $C-\varphi$ curve (Fig. 2). In the case of $(N(C_2H_5)_4)Br$, on going from a 0.01 $N$ solution to 0.1 $N$, a decrease in capacitance is observed in a certain range of potentials, while at strong negative polarizations the differential-capacitance curves in these solutions come closer together (Fig. 3). This phenomenon can be explained as follows. On going from KBr to $(N(C_2H_5)_4)Br$, an excess of undissociated $(N(C_2H_5)_4)Br$ dipoles

Fig. 3

Figure 3: Fig. 3

appears in the electrical double layer, displacing water molecules. Apparently, the corresponding decrease in the dielectric constant in the double layer leads to a decrease in capacitance in a certain range of potentials when the concentration of $(N(C_2H_5)_4)Br$ is increased. When butyl alcohol is added, clearly expressed minima near the p.z.c. appear on the $C-\varphi$ curves, as well as adsorption and desorption maxima.

The potentials of the minimum and of the adsorption maxima, as well as the capacitance values at these potentials, depend on the background cation, the concentration of butyl alcohol, and the concentration of the electrolyte (Figs. 2, 3, and 4). Thus, an increase in the amount of added alcohol decreases the capacitance at the minimum and

expands the interval of minimum potentials, and the adsorption and desorption maxima increase. The magnitude of these effects depends on the concentration of the electrolyte and of the background cations: at high background concentrations the capacitance at the minimum increases, and the interval of minimum potentials narrows. This phenomenon is associated mainly with increased adsorption of the anion $Br^-$ as the electrolyte concentration is increased. In this connection it is also necessary to take into account the different influence of the background cations on the adsorption of $Br^-$ ions. Increasing the amount of added butyl alcohol has a considerably smaller effect on the shape of the curve as the radius of the cation increases in the series

**Fig. 3.** Curves of differential capacitance at 750 Hz in solutions:
1 $-0.01\,N$ $(N(C_2H_5)_4)Br + 5.5 \cdot 10^{-2}\,M\,C_4H_9OH$,
2 $-0.1\,N$ $(N(C_2H_5)_4)Br + 5.5 \cdot 10^{-2}\,M\,C_4H_9OH$,
3 $-0.01\,N$ $(N(C_2H_5)_4)Br$,
4 $-0.1\,N$ $(N(C_2H_5)_4)Br$.

$$K^+ < (N(CH_3)_4)^+ < (N(C_2H_5)_4)^+ < (N(C_4H_9)_4)^+,$$

(Figs. 2, 3, and 4). At a corresponding ratio of the concentrations of butyl alcohol and the organic cation, the minimum on the $C-\varphi$ curve may be completely absent (curve 2 in Fig. 3 and curve 4 in Fig. 4).

According to Frumkin' s theory [10], desorption of an organic substance from the mercury surface should be the sharper, the greater the difference in capacitance in the pure background solution and in the solution with an addition of the organic substance. From the data of Fig. 1 it follows that desorption of butyl alcohol should be most sharply expressed against the KBr background. With an increase in the radius of the cation in the series

Figure 4: Differential-capacitance curves

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$$K^+ < (N(CH_3)_4)^+ < (N(C_2H_5)_4)^+ < (N(C_4H_9)_4)^+$$

the capacitance decreases and, consequently, desorption of butyl alcohol should be less pronounced. Indeed, as is seen from Fig. 4, the height of the desorption maximum decreases, and the maximum itself becomes flatter on going from $K^+$ to $(N(C_2H_5)_4)^+$, which corresponds to less pronounced desorption of butyl alcohol. In the case of the cation $(N(C_4H_9)_4)^+$, the maximum on the

of the $C$-$\varphi$ curve is completely absent and, consequently, the cations $(N(C_4H_9)_4)^+$, in agreement with theory, do not cause desorption of butyl alcohol. It is also possible that, in this case, van der Waals attraction between

**Fig. 4.** Differential-capacitance curves at 750 cps in solutions: $5.5 \cdot 10^{-1}$ $M$ $C_4H_9OH$ against the background of 0.01 $N$ solutions:
1 –KBr, 2 –$(N(CH_3)_4)Br$,
3 –$(N(C_2H_5)_4)Br$, 4 –$(N(C_4H_9)_4)Br$

hydrocarbon residues in the tetraalkylammonium ion and molecules of butyl alcohol plays a role.

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*Note: Figure translations are in progress. See original paper for figures.*