CESIUM AND SODIUM ION ADSORPTION ON PLATINUM FROM A MIXED ELECTROLYTE

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The study of ionic adsorption from mixed electrolytes has aroused great interest recently, because measurements under such conditions allow minute differences in the specific adsorbability of the ions to be established [1].

An attempt is made in the present work to describe the simultaneous adsorption of two ions on platinum on the basis of an approach used previously in studying the adsorption of two organic substances [2] or of one substance adsorbing in two different positions [3].

The system of isotherms for two adsorbing substances (1 and 2) can be written down in the form [3, 4]:

$$\left.\begin{aligned} b_1c_1 &= \frac{\theta_1}{n_1(1-\theta_1-\theta_2)^{n_1}}\exp(-2a_{11}n_1\theta_1-2a_{12}n_1\theta_2) \\ b_2c_2 &= \frac{\theta_2}{n_2(1-\theta_1-\theta_2)^{n_2}}\exp(-2a_{22}n_2\theta_2-2a_{12}n_2\theta_1) \end{aligned}\right\}, \quad (1)$$

where b_1 and b_2 are the adsorption equilibrium constants, c_1 and c_2 are the concentrations, θ_1 and θ_2 are the degrees of coverage, n_1 and n_2 are the ratios between the areas occupied by the particles of 1 and 2, and the area of the solvent molecules displaced by them, and the parameters a_{ij} characterize the interaction between the adsorbed particles: a_{11} for 1-1, a_{22} for 2-2, and a_{12} for 1-2 interaction. The relations

$$\left.\begin{aligned} \ln\beta_1c_1 &= \ln\Gamma_1+2B_{11}\Gamma_1+2B_{12}\Gamma_2 \\ \ln\beta_2c_2 &= \ln\Gamma_2+2B_{22}\Gamma_2+2B_{12}\Gamma_1 \end{aligned}\right\}, \quad (2)$$

where $\beta_1 = b_1\Gamma_m$; $\beta_2 = b_2\Gamma_m$; $\Gamma_m = n_1\Gamma_{1m} = n_2\Gamma_{2m}$;

$$B_{11} = \frac{n_1^2(1-2a_{11})}{2\Gamma_m}; \quad B_{22} = \frac{n_2^2(1-2a_{22})}{2\Gamma_m}; \quad B_{12} = \frac{n_1n_2(1-2a_{12})}{2\Gamma_m}; \quad (3)$$

and Γ_{1m} and Γ_{2m} are the maximum amounts adsorbed for particles 1 and 2, follow from the system of Eqs. (1) at relatively low coverages where $\ln(1-\theta_1-\theta_2) \approx -(\theta_1+\theta_2)$.

When the repulsive interaction between all adsorbed particles is sufficiently large, and Γ_1 and Γ_2 are not too small, one can neglect the quantities $\ln\Gamma_1$ and $\ln\Gamma_2$ in Eqs. (2), to a first approximation, and hence

$$\ln\beta_1c_1 = 2B_{11}\Gamma_1+2B_{12}\Gamma_2 \quad (4)$$

$$\ln\beta_2c_2 = 2B_{22}\Gamma_2+2B_{12}\Gamma_1\text{*}. \quad (5)$$

From Eqs. (4) and (5) one can obtain expressions for the dependence of Γ_1 on c_1 at c_2 = const, as well as for the dependences of Γ_1 on c_2 at c_1 = const or Γ_2 on c_1 at c_2 = const. Thus, in order to find the depend-

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*Equations (4) and (5) correspond to the Temkin isotherm for simultaneous adsorption of two substances in the region of intermediate coverages. When the repulsive interaction between all adsorbed particles is strong, these relations also extend to the region of low coverages, but not to overly low coverages.

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ence of Γ_1 on c_1 at c_2 = const one must extract Γ_2 from Eq. (5) and substitute it in Eq. (4). The result can be brought into the form

$$\ln \beta_1^{(2)} c_1 = 2B_{11}^{(2)} \Gamma_1, \tag{6}$$

where the apparent adsorption equilibrium constant $\beta_1{}^{(2)}$ and the apparent virial coefficient $B_{11}{}^{(2)}$ in the presence of component 2 are given by

$$B_{11}^{(2)} = B_{11} - B_{12}{}^2/B_{22} \tag{7}$$

and

$$\lg \beta_1^{(2)} = \lg \beta_1 - (B_{12}/B_{22}) \lg (\beta_2 c_2). \tag{8}$$

Thus, at c_2 = const there must be a linear dependence of Γ_1 on log c_1, where $B_{11}{}^{(2)}$ can be determined from the slope of this line while $\beta_1{}^{(2)}$ can be found by extrapolating it to its intersection with the abscissa. According to Eqs. (4) and (5), the individual adsorption isotherms of substances 1 and 2 can be represented, under the conditions being discussed, in the form

$$\lg \beta_1 c_1 = 2B_{11}\Gamma_1, \tag{9}$$

$$\lg \beta_2 c_2 = 2B_{22}\Gamma_2. \tag{10}$$

Therefore, the quantities B_{11} and B_{22} can be determined from the slope of the individual isotherms when plotted as Γ against log c, while β_1 and β_2 can be found by extrapolating the linear sections of these isotherms to their intersection with the abscissa. Knowing B_{11} and B_{22} one can calculate B_{12} from Eq. (7), and then log $\beta_1{}^{(2)}$ from Eq. (8). When the calculated and experimental values of $\beta_1{}^{(2)}$ coincide, it can be concluded that isotherms (1) and the assumptions employed above for the quantitative description of the simultaneous adsorption of two substances are appropriate.

In order to find the dependence of Γ_1 on c_2 at c_1 = const one must extract Γ_2 from Eq. (4) and substitute it in Eq. (5). The result can be brought into the form

$$\lg \cdot \beta_2{}^* c_2 = -2B_{12}{}^* \Gamma_1, \tag{11}$$

where

$$B_{12}{}^* = B_{11}B_{22} / B_{12} - B_{12} \tag{12}$$

and

$$\lg \beta_2{}^* = \lg \beta_2 - (B_{22} / B_{12}) \lg (\beta_1 c_1). \tag{13}$$

In a similar fashion one obtains the relation for the dependence of Γ_2 on c_1 at c_2 = const:

$$\ln \beta_1{}^* c_1 = -2B_{12}{}^* \Gamma_2, \tag{14}$$

where $B_{12}{}^*$ is given by Eq. (12) while

$$\lg \beta_1{}^* = \lg \beta_1 - (B_{11} / B_{12}) \lg (\beta_2 c_2). \tag{15}$$

It follows from Eqs. (11)-(15) that the linear sections of the Γ_1-log c_2 and Γ_2-log c_1 curves can be calculated on the basis of the quantities β_1, β_2, B_{11}, B_{22}, and B_{12}; their determination was already discussed above.

The relations found were experimentally tested at the Pt/Pt electrode, where the adsorption of Cs^+ (component 1) and Na^+ ions (component 2) from acidified cesium and sodium sulfate solutions was studied at the reversible hydrogen potential. The experiments were done at 20 ± 2°C following the technique of [5]. The experimental details were the same as in [6]. The adsorption isotherms of Na^+ and Cs^+ ions on platinum in 10^{-3} N H_2SO_4 + xN Na_2SO_4 (or Cs_2SO_4) have been measured before [6]. Additional measurements in the same systems were made in the present work for the adsorption of Cs^+ at low, and for the adsorption of Na^+ at high concentrations. The adsorption of Cs^+ ions was further measured for solutions of the composition 10^{-3} N H_2SO_4 + 10^{-2} N Na_2SO_4 + xN Cs_2SO_4.

The data obtained are reported in Fig. 1. It can be seen from the figure that the dependence of Γ_1 on log c_1 at c_2 = const is linear at intermediate coverages, as had to be expected from Eq. (6). A similar dependence is also observed on the initial sections of the adsorption isotherms of Cs^+ and Na^+ (curves 1 and 2), which represent the dependences of Γ_1 and Γ_2 on the concentration of the corresponding salts at constant

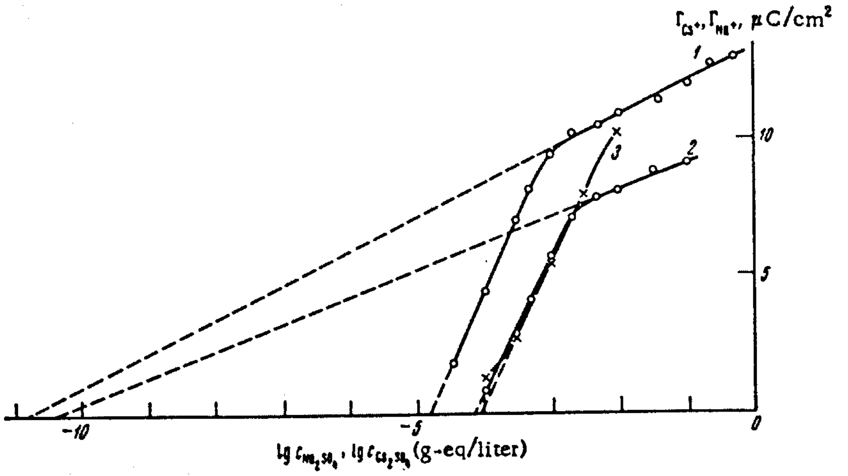

Fig. 1. The adsorption of Cs^+ (1 and 3) and Na^+ ions (2) as function of the concentration of Cs_2SO_4 and Na_2SO_4 at the reversible hydrogen potential in the solutions: 1) 10^{-3} N H_2SO_4 + xN Cs_2SO_4; 2) 10^{-3} N H_2SO_4 + xN Na_2SO_4; 3) 10^{-3} N H_2SO_4 + 10^{-2} N Na_2SO_4 + xN Cs_2SO_4.

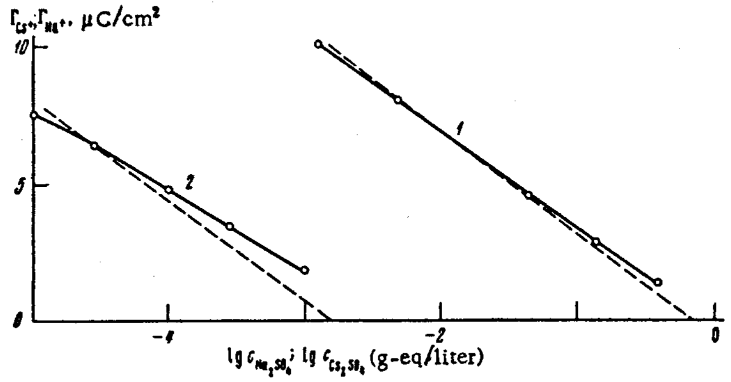

Fig. 2. Isotherms for the displacement of Cs^+ ions by Na^+ ions (1), and of Na^+ ions by Cs^+ ions at the reversible hydrogen potential in the solutions: 1) 10^{-3} N H_2SO_4 + $2 \cdot 10^{-3}$ N Cs_2SO_4 + xN Na_2SO_4; 2) 10^{-3} N H_2SO_4 + $2 \cdot 10^{-3}$ N Na_2SO_4 + xN Cs_2SO_4. The dashed lines are calculated according to Eqs. (11)-(15).

H_3O^+ ion concentration in solution. At higher salt concentrations the hydrogen ions are found to be completely expelled from the double layer, and we observe the individual adsorption isotherms of the Cs^+ and Na^+ ions [6].

The following values were obtained from the data of Fig. 1: $B_{11} = 1500$, $B_{22} = 1900$, and $B_{11}^{(2)} = 350$ Å²/ion; $\log \beta_1 = 10.8$; $\log \beta_1^{(2)} = 4.05$; $\log \beta_2 = 10.5$. The value of B_{12} calculated from Eq. (7) was 1460 Å²/ion. Calculation by Eq. (8) gives $\log \beta_1^{(2)} = 4.30$, which is sufficiently close to the experimental value of 4.05.

For the initial sections of the isotherms of Cs^+ and Na^+ when they are adsorbed jointly with H_3O^+ ions (component 3), one can write in accordance with the above:

$$B_{11}^{(3)} = B_{11} - B_{13}^2/B_{33}, \tag{16}$$

$$\lg \beta_1^{(3)} = \lg \beta_1 - (B_{13}/B_{33}) \lg(\beta_3 c_3), \tag{17}$$

$$B_{22}^{(3)} = B_{22} - B_{23}^2/B_{33}, \tag{18}$$

$$\lg \beta_2^{(3)} = \lg \beta_2 - (B_{23}/B_{33}) \lg(\beta_3 c_3). \tag{19}$$

The quantities β_i and B_{jj} represent the apparent adsorption equilibrium constants and the apparent virial coefficients in the presence of hydrogen ions. From Eqs. (16) and (18) follows $B_{13} = \sqrt{B_{33}(B_{11} - B_{11}^{(3)})}$ and $B_{23} = \sqrt{B_{33}(B_{22} - B_{22}^{(3)})}$. When these relations are now substituted into Eqs. (17) and (19) it is found that

$$\frac{\lg(\beta_3 c_3)}{\sqrt{B_{33}}} = \frac{\lg \beta_1 - \lg \beta_1^{(3)}}{\sqrt{B_{11} - B_{11}^{(3)}}} = \frac{\lg \beta_2 - \lg \beta_2^{(3)}}{\sqrt{B_{22} - B_{22}^{(3)}}}\ . \tag{20}$$

Experimentally it was found that $\log \beta_2^{(3)} = 4.15$; $\log \beta_1^{(3)} = 4.80$; $B_{22}^{(3)} = 360$; and $B_{11}^{(3)} = 350$ Å^2/ion. Thus, $\frac{\lg \beta_1 - \lg \beta_1^{(3)}}{\sqrt{B_{11} - B_{11}^{(3)}}} = 0.175$ and $\frac{\lg \beta_2 - \lg \beta_2^{(3)}}{\sqrt{B_{22} - B_{22}^{(3)}}} = 0.163$, i.e., in harmony with Eq. (20) these values are sufficiently close. In this case we have tested the theory in a more complicated way by using the isotherms for the joint adsorption of Cs^+ or Na^+ ions with H_3O^+ ions.

To test relations (11)-(15) we have measured the adsorption of Cs^+ ions as function of Na_2SO_4 concentration in 10^{-3} N $H_2SO_4 + 2 \cdot 10^{-3}$ N $Cs_2SO_4 + x$N Na_2SO_4, and that of Na^+ ions as function of Cs_2SO_4 concentration in 10^{-3} N $H_2SO_4 + 2 \cdot 10^{-3}$ N $Na_2SO_4 + x$N Cs_2SO_4. The results of these measurements are shown in Fig. 2; also given there are the straight-line sections of the Γ_1-log c_2 and Γ_2-log c_1 curves calculated according to Eqs. (11)-(15). It can be seen from the figure that the calculation is in satisfactory agreement with experiment. The strong relative displacement between curves 1 and 2 of Fig. 2 reflects the effect of specific adsorption of the Cs^+ ions on the Pt/Pt electrode [6-9]. The data given in Fig. 2 show clearly the advantages of studying the adsorption from mixed electrolytes in order to compare the adsorbabilities of different ions.

Thus, the relations deduced above are confirmed by the experimental data obtained.

It is of special interest to ask for the interaction parameters of the adsorbed ions: a_{11}, a_{22}, and a_{12}. It follows from Eq. (3) that their values can be found when Γ_m, n_1, and n_2 are known. These values are not at our disposal, however, for the system studied. One can only deduce, therefore, the relation between the values of a_{11}, a_{22}, and a_{12}. To this end we shall consider the ratios between the virial coefficients B_{11}/B_{12} and B_{22}/B_{12}. Taking into account that repulsion forces will prevail between the adsorbed cations, and hence $a_{ij} < 0$, we can conveniently compare their absolute values. Thus we find from Eq. (3):

$$\frac{B_{11}}{B_{12}} = \frac{1 + 2|a_{11}|}{k(1 + 2|a_{12}|)} \text{ and } \frac{B_{22}}{B_{12}} = \frac{k(1 + 2|a_{22}|)}{1 + 2|a_{12}|}$$

where $k = n_2/n_1$. Since, according to our data, $B_{11} : B_{12} : B_{22} = 1.03 : 1 : 1.3$, we have $|a_{11}| = 1.03k - 1/2 + 1.03k\,|a_{12}|$ and $|a_{22}| = (1.30 - k)/2k + 1.3\,|a_{12}|/k$. The value of k can be estimated, to a first approximation, from the ratio $\Gamma_1 : \Gamma_2$ at 1 N concentrations of Cs^+ and Na^+ ions in solution, which is 1.34. Hence follows $|a_{11}| > |a_{12}| > |a_{22}|$, which does not coincide with the order of variation of the virial coefficients B_{ij}. This is so because the virial coefficients reflect, not only the interaction between the adsorbed particles but steric effects as well, which are caused by the finite size of the adsorbate particles. Therefore, a conclusion as to the interaction between particles in the surface layer which has been inferred on the basis of the B_{ij} values will not always be correct.

The decrease in the repulsive interaction when going from Cs^+ to Na^+, which was obtained in the present work, has also been observed by Palm and coworkers [10] in the case of a Bi electrode. This was explained by a screening effect of the diffuse-layer anions which will be more pronounced the smaller the distance between inner and outer Helmholtz plane. In other words, the diffuse-layer anions weaken the repulsive interaction to a larger extent in the adsorption of Na^+ ions, which are not so strongly attracted to the electrode surface as are the Cs^+ ions. Of course, such an explanation is strictly valid only when partial charge transfer from the adsorbed ion to the electrode surface is absent. It must be noted in conclusion that the virial coefficients for Cs^+ and Na^+ ions on platinum are substantially larger in absolute value than they are on bismuth or mercury. To a considerable degree this seems to be due to the inhomogeneous character of the Pt/Pt electrode surface.

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