SIMULTANEOUS ADSORPTION OF CESIUM AND SODIUM CATIONS ON PLATINIZED PLATINIUM

V. E. Kazarinov and O. A. Petrii

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Using the radioactive indicator method, we have investigated adsorption of Cs^+ and Na^+ cations from solutions of 10^{-2} N $(Cs_2SO_4 + Na_2SO_4) + 10^{-3}$ N H_2SO_4 at the reversible hydrogen potential ($\varphi_r = 0$) and from 10^{-2} N solutions of (NaOH + CsOH) at different potentials. When $\varphi_r = 0$, preferential adsorption of Cs^+ ions is observed. In an alkaline solution, preferential adsorption of Na^+ ions is observed on oxidized platinum.

From the data thus obtained we calculated the selective adsorption constant $K_S = (\Gamma_{Cs^+}/\Gamma_{Na^+}) \times (c_{Na^+}/c_{Cs^+})$, where Γ_{Cs^+} and Γ_{Na^+} are respectively the Cs^+ and Na^+ adsorption values, and c_{Cs^+} and c_{Na^+} are their concentrations in the mixture. The value of K_S depends on the potential, the solution pH, and the concentration ratio c_{Cs^+}/c_{Na^+}, and decreases with an increase in the latter.

The experimental data were processed by two methods: by the formal thermodynamics used for describing adsorption on ion exchangers, and by means of Temkin and Frumkin isotherms for a mixture of two substances.

Quantitative data characterizing the relation between adsorption of Cs^+ and Na^+ cations (specifically adsorbed on a platinum electrode [1-7]) are necessary for understanding the structure of the double electric layer. Such data may also be of independent interest as regards selectivity in the theory of ion-exchange processes. When platinized platinum is used as the adsorbent, the factors governing selectivity become revealed more readily because, if the concentrations are not too low, diffusion limitations are than virtually absent and swelling of the adsorbent is excluded. Furthermore, one may also affect the selectivity of the process by controlled change of the interface potential.

We investigated simultaneous adsorption of Cs^+ and Na^+ cations on a platinized platinum electrode in an acid (pH 3) 10^{-2} N solution of $(Cs_2SO_4 + Na_2SO_4)$ at the reverse hydrogen potential and in an alkaline solution of 10^{-2} N (CsOH + NaOH) at various different potentials. The adsorption value was determined by means of Cs^{134} and Na^{22} isotopes, the procedure being the same as described in [8]. The electrode preparation conditions, the method for determining the true surface, and the solution preparation procedure were the same as described in our previous communications, for example, in [1, 5]. The experiments were performed at room temperature (20 ±3°C). The potentials φ_r are relative to a reversible hydrogen electrode in the same solution. The order of the experiments was as follows. Solutions containing Cs^+ and Na^+ cations were poured successively into the cell in a specific ratio. In the first series of experiments the solutions were labeled with radioactive cesium, the second series with radioactive sodium.

The electrode potential was measure by a P-5827 potentiostat, but in the case of measurements at the reversible hydrogen potential we saturated the solution with hydrogen. The electrode was kept in the solution of given composition for 15 min. Special experiments showed that, in agreement with [9], this period was sufficient to establish adsorption equilibrium. Owing to the high process rate (~ 90% in 5 min), quantitative investigation of the exchange kinetics by this procedure was impossible.

Particular interest is attached to the exchange kinetics of adsorbed Cs^+ ions on Na^+ cations at $\varphi_r = 0$ and of adsorbed Na^+ cations on Cs^+ cations on oxidized platinum in alkaline solutions, i.e., as will be shown below, the exchange kinetics of preferentially adsorbed cations on less strongly adsorbed cations. In these

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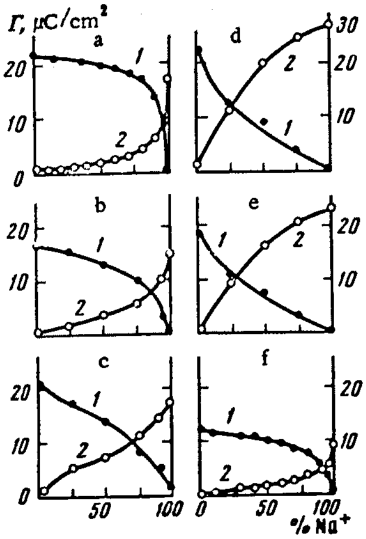

Fig. 1. Γ_{Cs^+} (1) and G_{Na^+} (2), plotted vs solution composition: a-e) 10^{-2} N MeOH: a) $\varphi_r = 0$; b) $\varphi_r = 0.55$; c) $\varphi_r = 1.1$; d) preliminarily anodically oxidized electrode in a solution of 10^{-2} N NaOH (CsOH) by a current of 5 mA/cm³ for 10 min; e) electrode preliminarily anodically oxidized in 0.1 N H_2SO_4, as in previous case; f) 10^{-2} N (Na_2SO_4 + Cs_2SO_4) + 10^{-3} H_2SO_4; $\varphi_r = 0$.

cases, after rapid exchange of the bulk of the adsorbed cations on the electrode surface, 10-15% of the initially adsorbed cations remains, even after 30 min. An explanation of this requires a special investigation. Bearing in mind our previous remarks, in the investigation of coadsorption of Cs^+ and Na^+ ions the experiments were always begun with solutions containing an excess of less strongly adsorbed ions.

The experimental data are given in Fig. 1 a-f. The data of Fig. 1c were obtained at an electrode, the potential of which was brought from $\varphi_r = 0$ to $\varphi_r = 1.2$ V in a solution of 10^{-2} N CsOH (NaOH) with a current of 0.1 mA/cm² on the visible surface. Thirty minutes after the current was switched off, the potential was established at ~1.1 V and its subsequent rate of displacement during purging of the cell with argon was less than 0.5 mV/min. As follows from the charging curves, such an electrode state is characterized by coverage of ~50% of the Pt surface atoms by adsorbed oxygen. The data of Fig. 1 d-e were obtained for electrodes preliminarily oxidized in a CsOH (NaOH) solution or in 0.1 N H_2SO_4 at oxygen evolution potentials. A change in the current density in the range 0.1-1 mA/cm² on the visible surface, and of the duration of polarization in the range 10-60 min, had no effect on the adsorption measurements. Such electrode preparation corresponds to approximately monolayer coverage of the platinum surface by adsorbed oxygen. The residence time of the electrodes after switching off the polarization in CsOH and NaOH solutions reached 30 min, which was necessary to attain steady values of Cs^+ and Na^+ adsorption.

It will be seen from Fig. 1 that in both alkaline and acid solutions, at the reversible hydrogen potential we observe preferential adsorption of cesium cations. In an alkaline solution, as the potential changes toward the anode side, the difference between the adsorbabilities of Cs^+ and Na^+ cations begins to decrease, and preferential adsorption of sodium cations is already observed on an electrode oxidized at oxygen evolution potentials. The results shown in Figs. 1a and 1f were briefly discussed and compared with analogous data for a mercury electrode in [7].

Let us examine the experimental data from the viewpoint of ionic equilibria. From the equation of electrochemical potentials of ions of the same type in the adsorbed state, $(\tilde{\mu})$*, and in solution, $(\bar{\mu})$, and from the equation for electrochemical potential in the form

$$\mu_i = \mu_i^0 + RT \ln a_i + z_i F\varphi, \tag{1}$$

where a_i is the ionic activity, z_i is the valence, μ_i^0 is the standard chemical potential, when $z_i = 1$ it follows that

$$\tilde{\mu}^0_{Cs^+} + RT \ln \bar{a}_{Cs^+} - \mu^0_{Cs^+} - RT \ln a_{Cs^+} = -F\Delta\varphi_{Cs^+}, \tag{2}$$

$$\tilde{\mu}^0_{Na^+} + RT \ln \tilde{a}_{Na^+} - \mu^0_{Na^+} - RT \ln c_{Na^+} = -F\Delta\varphi_{Na^+}. \tag{3}$$

The potentials $\Delta\varphi_{Cs^+}$ and $\Delta\varphi_{Na^+}$ correspond to the potentials of the planes in which these ions are adsorbed, with respect to the potential in the bulk of the solution (the ψ' potential). Subtracting Eq. (3) from Eq. (2) and making simple transformations, we get

$$\frac{\bar{a}_{Cs^+} a_{Na^+}}{\bar{a}_{Na^+} a_{Cs^+}} = \exp\left[\frac{\tilde{\mu}^0_{Cs^+} + \tilde{\mu}^0_{Na^+} - \mu^0_{Cs^+} - \mu^0_{Na^+}}{RT}\right] \times \exp\left[-\frac{F(\Delta\varphi_{Cs^+} - \Delta\varphi_{Na^+})}{RT}\right] = K \exp\left[-\frac{F(\Delta\varphi_{Cs^+} - \Delta\varphi_{Na^+})}{RT}\right], \tag{4}$$

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*Here and below, symbols with a wavy line above them denote adsorbed ions.

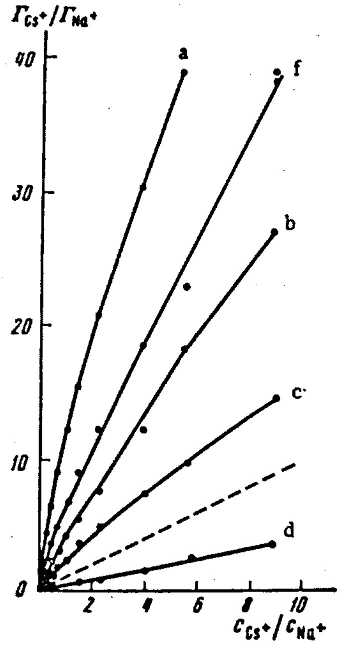

Fig. 2

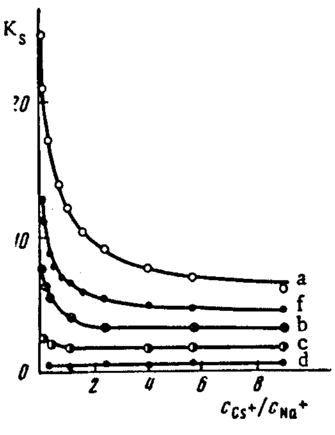

Fig. 3

Fig. 2. Ratio $\Gamma_{Cs^+}/\Gamma_{Na^+}$ plotted vs c_{Cs^+}/c_{Na^+}. Notation same as in Fig. 1. The dashed line is a plot of $\Gamma_{Cs^+}/\Gamma_{Na^+}$ vs c_{Cs^+}/c_{Na^+} for an ideal system.

Fig. 3. K_s plotted vs ratio of Cs^+ and Na^+ ionic concentrations in the solution. Notation same as in Fig. 1.

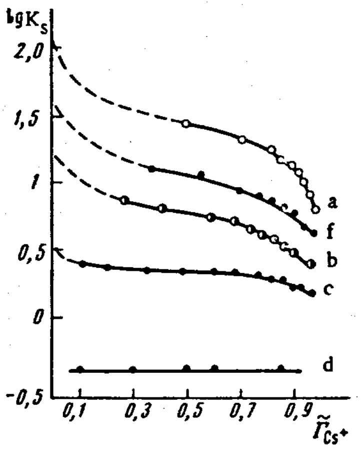

Fig. 4. Log K_s vs $\tilde{\Gamma}_{Cs^+}$. Notation same as in Fig. 1.

where K is the thermodynamic equilibrium constant. Since the experiments were performed at constant ionic strength in relatively dilute solutions, the ionic activities in the solution may be replaced by the concentrations. The activities of the ions in the adsorbed state are replaced by the product of the activity coefficients $\tilde{f}'$ by the surface concentration. Hence

$$\frac{f'_{Cs^+}}{f'_{Na^+}}\,\frac{\Gamma_{Cs^+}c_{Na^+}}{\Gamma_{Na^+}c_{Cs^+}} = K\exp\left[-\frac{F}{RT}\left(\Delta\varphi_{Cs^+}-\Delta\varphi_{Na^+}\right)\right]. \tag{5a}$$

The method of expressing the volumetric and surface concentrations is irrelevant because they are present in Eq. 5a as ratios. Transposing the activity coefficients to the right-hand side of Eq. 5a, we get

$$\frac{\Gamma_{Cs^+}}{\Gamma_{Na^+}}\,\frac{c_{Na^+}}{c_{Cs^+}} = K\,\frac{\tilde{f}'_{Na^+}}{\tilde{f}'_{Cs^+}}\exp\left[-\frac{F}{RT}\left(\Delta\varphi_{Cs^+}-\Delta\varphi_{Na^+}\right)\right]. \tag{5b}$$

The left hand part of Eq. (5b) can be determined directly by experiment. However, a quantitative verfification of Eq. (5b) is at present impossible because the specific form of the exponential term and the ratio $\tilde{f}_{Na^+}/\tilde{f}_{Cs^+}$ are unknown. A verification is apparently only possible after further development of the theory of the double electric layer formed by specifically adsorbed ions of two types. The experimental data were therefore processed by the procedure used in the theory of ion-exchange equilibria, namely Eq. (5b) was written in the form

$$\frac{\Gamma_{Cs^+}\tilde{f}_{Cs^+}}{\Gamma_{Na^+}\tilde{f}_{Na^+}}\,\frac{c_{Na^+}}{c_{Cs^+}} = K. \tag{6}$$

In this equation

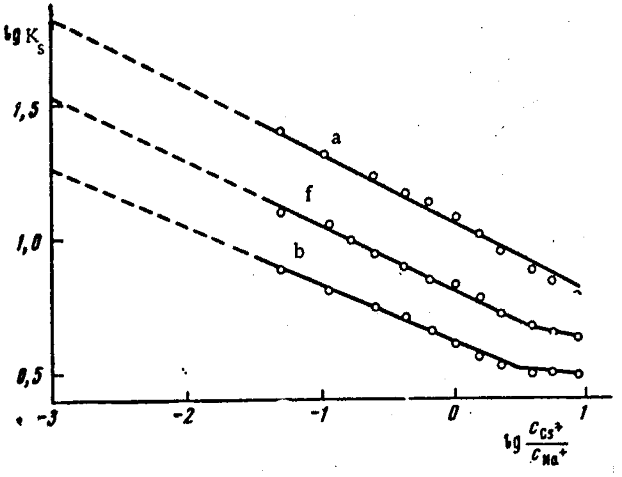

Fig. 5. Log Ks plotted vs log c_{Cs^+}/c_{Na^+}. Notation same as in Fig. 1.

$$\tilde{f}_{Cs^+} = \tilde{f}'_{Cs^+} \exp\left[\frac{F}{RT}\Delta\varphi_{Cs^+}\right], \text{ a } \tilde{f}_{Na^+} = \tilde{f}'_{Na^+}\left[\exp\frac{F}{RT}\Delta\varphi_{Na^+}\right].$$

Thus $\tilde{f}_{Cs^+}$ and $\tilde{f}_{Na^+}$ also reflect the difference between the plane potentials of the adsorption of differentions. Equation (6) may be regarded as the adsorption isotherm of two substances. Deviations from the Henry isotherm are formally taken into account by introducing the activity coefficients.

Equation (6) is written in the form

$$\frac{\Gamma_{Cs^+}}{\Gamma_{Na^+}}\,\frac{c_{Na^+}}{c_{Cs^+}} = K\frac{\tilde{f}_{Na^+}}{\tilde{f}_{Cs^+}} = K_s. \tag{7}$$

The value of K_s, the selectivity constant, can be calculated from the experimental data. The marked dependence of K_s on c_{Cs^+}/c_{Na^+} (Figs. 2, 3) indicates deviation of the properties of this system from an ideal system, and also that $\tilde{f}_{Na^+}$ and $\tilde{f}_{Cs^+}$ depend on Γ_{Na^+} and Γ_{Cs^+}.

As shown in [10], the properties of such a system may be analyzed by means of the Gibbs-Duhem equation and by selecting a standard state for the adsorbed ions, different from that for ions in solution.* In this case $\tilde{f}_{Me^+}$ is taken as 1 at complete coverage of the surface by ions of the given type. In our system this state corresponds to the presence in solution (and therefore on the electrode) of only Cs^+ or Na^+ ions. Such an approach enables one to calculate the thermodynamic exchange constant K, and also the dependence of $\tilde{f}_{Me^+}$ on surface coverage by ions of given type. For our system†, such relationships have the form

$$\ln K = \int_0^1 \ln K_s\, d\tilde{\Gamma}_{Cs^+}, \tag{7}$$

$$\ln \tilde{f}_{Cs^+} = -(1-\tilde{\Gamma}_{Cs^+})\ln K_s - \int_{\Gamma_{Cs^+}}^{1} \ln K_s\, d\tilde{\Gamma}_{Cs^+}, \tag{8}$$

$$\ln \tilde{f}_{Na^+} = \tilde{\Gamma}_{Cs^+} \ln K_s - \int_0^{\tilde{\Gamma}_{Cs^+}} \ln K_s\, d\tilde{\Gamma}_{Cs^+}, \tag{9}$$

where $\tilde{\Gamma}_{Me^+}$ denotes the mole fraction of the given cation in the adsorbed state;

$$\tilde{\Gamma}_{Cs^+} = \frac{\Gamma_{Cs^+}}{\Gamma_{Cs^+}+\Gamma_{Na^+}};$$

$$\tilde{\Gamma}_{Na^+} = \frac{\Gamma_{Na^+}}{\Gamma_{Na^+}+\Gamma_{Cs^+}};$$

$$\tilde{\Gamma}_{Cs^+} + \tilde{\Gamma}_{Na^+} = 1.$$

Figure 4 plots log K_s vs $\tilde{\Gamma}_{Cs^+}$. The solid lines are the curves obtained by direct calculation from the experimental data. Although possible in principle, measurements of the adsorption values of cesium cations at low ($< 5 \cdot 10^{-4}$ M) concentrations involve specific experimental difficulties. To determine the dependence of Γ_{Cs^+} on log K_s in the Γ_{Cs^+} region where direct measurements of Γ_{Cs^+} were not made, we therefore used the following procedure.

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*A detailed exposition of such an approach to the exchange thermodynamics is given, for example, in [11-15].

†In contrast with the system examined in [10], our system is not a two-component system, but a polycomponent one, and the total amount of adsorbed ions does not remain strictly constant. However, the first factor is of no significance because all the experiments were performed at constant potential (φ_r = const) and constant ionic strength of the solution, therefore the corresponding terms in the Gibbs adsorption equation become zero. The second factor is more significant, but, bearing in mind that the change in the charge is small, Eqs. (7), (8), and (9) may be regarded as a first approximation.

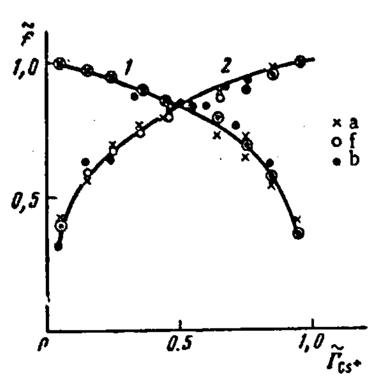

Fig. 6

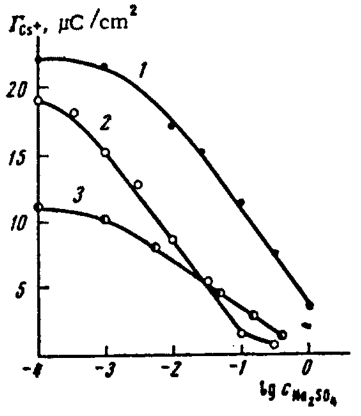

Fig. 7

Fig. 6. $\tilde{f}_{Cs^+}$ (1) and $\tilde{f}_{Na^+}$ (2), plotted vs $\tilde{\Gamma}_{Cs^+}$; a, b, f were plotted for the same conditions as in Fig. 1.

Fig. 7. Γ_{Cs^+} plotted vs logarithm of the concentration: 1) 10^{-2} N CsOH + xNa$_2$SO$_4$, $\varphi_r = 0$; 2) in the same solution on an electrode preliminarily oxidized in acid; 3) $2 \cdot 10^{-3}$ N Cs$_2$SO$_4$ + xN Na$_2$SO$_4$, $\varphi_r = 0$, pH = 3.

It will be seen from Fig. 5 that to a first approximation a linear relation exists between log K_s and log (c_{Cs^+}/c_{Na^+}) in a wide range of log (c_{Cs^+}/c_{Na^+}). The latter was extrapolated to the region of low cesium concentrations (the dashed sectors of the straight lines). Then, assigning values to K_s and finding the ratio c_{Cs^+}/c_{Na^+}, from the ratio $(\Gamma_{Cs^+} c_{Na^+}/\Gamma_{Na^+} c_{Cs} = K_s)$, we determined the mole fraction of cesium cations in the adsorbed state, $\tilde{\Gamma}_{Cs^+}$, at the given K_s. The dependence thus obtained are represented by the dashed sectors of the curves in Fig. 4. The values of $\tilde{f}_{Cs^+}$ and $\tilde{f}_{Na^+}$ for different $\tilde{\Gamma}_{Cs^+}$ were then calculated from Eqs. (8) and (9). The results are given in Fig. 6. It is of interest that the adsorption potential has little effect on the dependences of $\tilde{f}_{Cs^+}$ and $\tilde{f}_{Na^+}$ on $\tilde{\Gamma}_{Cs^+}$.

Thus the introduction of the activity coefficients of the ions in the absorbed state enables one to describe quantitatively the adsorption isotherm of two ions on a platinum electrode.

From the analytical expression of the data of Fig. 5 in the form

$$\lg K_s = \lg K' - \alpha \lg (c_{Cs^+}/c_{Na^+}) \qquad (10)$$

and the expression for $K_s = (\Gamma_{Cs^+}/\Gamma_{Na^+})(c_{Na^+}/c_{Cs^+})$, we can obtain an empirical equation for the adsorption isotherm:

$$\Gamma_{Cs^+}/\Gamma_{Na^+} = K' (c_{Cs^+}/c_{Na^+})^{1-\alpha}.$$

This equation is similar to the Baedeker-Freundlich equation, widely used for investigation of ion exchange [14].

Calculating the thermodynamic equilibrium constant from Eq. (7), we can find the standard free energy of exchange $\Delta G = -RT \ln K$, i.e., the energy gain obtained by replacement of one mole of adsorbed Cs$^+$ cations. It was found that in the case of a solution [10^{-2} N (Cs$_2$SO$_4$ + Na$_2$SO$_4$) + 10^{-3} N H$_2$SO$_4$, $\Delta G = -1.5$ kcal/mole] and in the case of a 10^{-2} N alkaline solution 1.9 kcal/mole when $\varphi_r = 0$; -1.1 kcal/mole when $\varphi_r = 0.55$ V; -0.5 kcal/mole when $\varphi_r = 1.1$ V; and $+0.5$ kcal/mole when $\varphi_r = 1.3$ V.

For average values of Γ_{Cs^+}, to a first approximation a linear relation exists between log K_s and Γ_{Cs^+}. This means that the free energy of exchange of adsorbed Na$^+$ cations for Cs$^+$ cations decreases linearly with the mole fraction of Cs$^+$ cations on the platinum surface. Thus in our system we have a relationship similar to that observed during adsorption on surfaces, the properties of which are described by means of the model of a uniformly inhomogeneous surface or that of repulsive interaction (the Temkin isotherm).

It is of interest to examine the experimental data as adsorption isotherms of a mixture of two substances. Temkin [16] has already undertaken this (he does not give the precise form of repulsive interaction). The equations obtained have the form

$$\theta_1 = \frac{a_{22}}{\Delta} \ln B_1c_1 - \frac{a_{12}}{\Delta} \ln B_2c_2, \tag{12}$$

$$\theta_2 = \frac{a_{11}}{\Delta} \ln B_2c_2 - \frac{a_{12}}{\Delta} \ln B_1c_1, \tag{13}$$

where θ_1 and θ_2 are respectively the degrees of surface coverage by the first and second substances, B_1, B_2, c_1, and c_2 are respectively the adsorption equilibrium constants and concentrations (pressures) of the first and second substances, a_{11}, a_{12}, and a_{22} are coefficients characterizing mutual repulsive interaction of the particles, and $\Delta = a_{11} \cdot a_{22} - a_{12}$. Here and below the subscript 1 relates to a Cs^+ cation, the subscript 2 to an Na^+ cation. Dividing Eqs. (12) and (13) by one another, we get

$$\frac{\theta_1}{\theta_2} = \frac{\Gamma_1\Gamma_2^\infty}{\Gamma_2\Gamma_1^\infty} = \frac{\Gamma_1}{\Gamma_2} K = \frac{a_{22} \ln B_1c_1 - a_{12} \ln B_2c_2}{a_{11} \ln B_2c_2 - a_{12} \ln B_1c_1}, \tag{14}$$

where Γ_1^∞ and Γ_2^∞ are the limiting surface coverages by Cs^+ and Na^+ cations, respectively. Solution of Eq. (14) gives us five constants: B_1, B_2, a_{11}, a_{12}, and a_{22}. However, the absolute values of Γ_1^∞ and Γ_2^∞ remain indeterminate, because the solution of the equation gives their ratio K. As shown by calculations, the data of Fig. 1a-b and f are satisfactorily described by an equation like (14).

We made an attempt to examine the experimental data by means of the Frumkin isotherms for a mixtures of two substances [17, 18]. In the presence of repulsive interaction the isotherm has the form

$$B_1c_1 = \frac{\theta_1}{1 - \theta_1 - \theta_2} \exp[2a_{11}\theta_1 + 2a_{12}\theta_2], \tag{15}$$

where the notation is the same as in Eq. (14). Dividing by one another the equations of type (15) for sodium ions and cesium ions, we get

$$\frac{B_1c_1}{B_2c_2} = \frac{\theta_1}{\theta_2} \exp\{2[a_{11}\theta_1 + a_{12}(\theta_2 - \theta_1) - a_{22}\theta_2]\}. \tag{16}$$

By transformation, we get

$$\frac{\theta_2c_1}{\theta_1c_2} = \frac{\Gamma_2c_1\Gamma_1^\infty}{\Gamma_1c_2\Gamma_2^\infty} = \frac{\Gamma_2c_1}{\Gamma_1c_2} K = \frac{B_2}{B_1} \exp\{2[a_{11}\theta_1 + a_{12}(\theta_2 - \theta_1) - a_{22}\theta_2]\}. \tag{17}$$

As stated above, the value of $\Gamma_2c_1/\Gamma_1c_2 = K_S$ is readily determined from the experimental data, a linear relation between log K_S and $\tilde{\Gamma}_{Cs^+}$ being observed for average values of $\tilde{\Gamma}_{Cs^+}$. Such a dependence agrees with Eq. (17). In fact, if we replace θ_1 and θ_2 by the mole fraction of Cs^+ and Na^+ cations in the adsorbed state, when $\tilde{\Gamma}_{Cs^+} \approx \tilde{\Gamma}_{Na^+} \approx 0.5$, the middle term of the exponent may be disregarded, and hence

$$K_s = \frac{B_2}{B_1} K' \exp\{2a_{11}\tilde{\Gamma}_1 - a_{22}\tilde{\Gamma}_2 - a_{22}\tilde{\Gamma}_2\}(\theta_1 + \theta_2).$$

Since $\tilde{\Gamma}_1 = 1 - \tilde{\Gamma}_2$ and $\theta_1 + \theta_2 = 1$, we get

$$K_s = \frac{B_1}{B_2} K'' \exp\{2[a_{11}\tilde{\Gamma}_1 - a_{22}(1 - \tilde{\Gamma}_1)]\} = \frac{B_1}{B_2} K' \exp\{2[\tilde{\Gamma}_1(a_{11} + a_{22}) - a_{22}]\}. \tag{18}$$

Hence it follows that when $\tilde{\Gamma}_1 \simeq \tilde{\Gamma}_2$,

$$\lg K_s \simeq \text{const} - k\tilde{\Gamma}_1. \tag{19}$$

It follows from approximate equation (19) that when the concentration of the first substance (Cs^+) remains constant and that of the second substance (Na^+) increases, $\tilde{\Gamma}_1$ must decrease linearly as log c_2 increases:

$$\lg K_s = \lg \frac{\tilde{\Gamma}_1c_1}{\tilde{\Gamma}_2c_2} = \lg \frac{\tilde{\Gamma}_1}{\tilde{\Gamma}_2} + \lg c_2 - \lg c_1.$$

Since with $\Gamma_1 \simeq \Gamma_2$, $\log(\Gamma_1/\Gamma_2) \approx 0$, and $\log c_1 = \text{const}$, we may write

$$\text{const}_2 + \lg c_2 = \text{const}_3 - k_1\tilde{\Gamma}_1$$

or

$$\tilde{\Gamma}_1 = \text{const} - k_1' \lg c_2. \tag{20}$$

A similar equation is derived directly from Temkin equations (12) and (13). The presence of a linear dependence between Γ_{Cs^+} and $\log c_{Na_2SO_4}$ is confirmed by Fig. 7.*

The ratios $a_{11} : a_{12} : a_{22}$, calculated from Eq. (14) and from Eq. (16) for the case in Fig. 1f, showed close mutual agreement and were 1.0 : 1.2 : 1.3. Such a result agrees with the conclusions drawn from an examination of the individual adsorption isotherms of Cs^+ and Na^+ cations at pH 3 [5]. It follows from this report that the ratio of the coefficients in the isotherm equation $\Gamma = \text{const} + (1/f)\ln c$ for Cs^+ and Na^+ cations is also close to 1:1.3. The increase in f as one goes from Cs^+ to Na^+ is due to the more marked charge transfer for specific adsorption of Cs^+.

Note, however, that this ratio $a_{11} : a_{12} : a_{22}$ characterizes the so-called effective mutual repulsion of adsorbed particles, because it was obtained without taking account of the areas occupied by ions in the adsorbed state. A more detailed analysis of the physical meaning of the a values, given in [20], shows that "true" repulsion between adsorbed particles increases in the sequence

$$Na^+ \leftrightarrow Na^+ < Na^+ \leftrightarrow Cs^+ < Cs^+ \leftrightarrow Cs^+.$$

Thus data on adsorption of Cs^+ and Na^+ cations on an electrode in relation to the solution composition may be represented satisfactorily both by introducing the activity coefficients of ions in the adsorbed state and by means of isotherms of specific form, namely Temkin and Frumkin isotherms.

To explain the change in selectivity in the sequence Cs^+ and Na^+ with the electrode potential in an alkaline solution, we must make certain assumptions on the model of the double electric layer and on the adsorption mechanism of the ions.† A comparison of the adsorption values of Cs^+ and Na^+ cations at the reversible hydrogen potential shows that the charge on the double electric layer formed by Cs^+ cations is approximately 25% greater; this might be due to the smaller size of hydrated Cs^+ cations and to the presence of their specific reaction with platinum [3-7]. Thus the preferential adsorption of Cs^+ cations on reduced platinum may be explained by the same ideas as those developed for the explanation of the data obtained at a mercury electrode [23-25].

In accordance with our previous assumption [21, 26], for oxidized platinum we must assume that the negative charge is concentrated on adsorbed oxygen. The latter is incorporated more readily into the coordination sphere of the Na^+ cation than in the case of the Cs^+ cation, probably owing to the stronger interaction with Na^+ cations, which are smaller in dehydrated form. The gradual change in the selectivity constant as one goes from reduced to oxidized platinum must be attributed to a change in the adsorption mechanism with increasing accumulation of adsorbed oxygen on the surface.

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*A similar dependence was obtained by Mosevich et al. [19] on platinized carbon.

†Our previous communications [21, 22] indicated a possible relative change in the order of adsorbability of Cs^+ and Na^+ cations in an alkaline solution on reduced and oxidized platinum.

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