Adsorption of Cations on Platinized Charcoal in a Hydrogen Atmosphere

By *S. Petrov, R. Burstein* and *P. Kisseleva*

In a number of investigations of this laboratory[1] it has been shown that activated charcoal in solutions of electrolytes behaves like a gas electrode. When charcoal is saturated with oxygen it acquires a positive charge in the solution and adsorbs anions from the solution of the electrolyte; but when it contains small amounts of platinum and is saturated with hydrogen it is charged negatively and adsorbs cations from the solution. The solution in the latter case becomes acidulated.

In the present work the influence of valency and atomic weight of cations on their adsorption by activated charcoal in a hydrogen atmosphere was investigated. We investigated the adsorption of the following cations from solutions of their respective chlorides: lithium, sodium, potassium, barium, cadmium, lanthanum, thorium and thallium from thallium nitrate. All the solutions except thallium nitrate were 0.01 *N* with respect to HCl. The salt concentration *c* in the solution varied from 0.01 to 1 *N*. The charcoal was kept in sealed ampoules in a hydrogen atmosphere. In the adsorption bulb *A* (Fig. 1) 0.5 gr. of charcoal was placed, then 10 cm.^{3} of the electrolyte solution were added. The adsorption bulb was connected by a ground

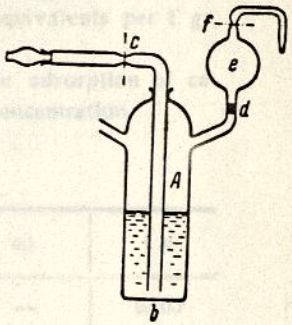

Fig. 1.

[1] Bruns a. Frumkin, Z. physik. Chem., **141**, 171 (1929).

joint with the apparatus which served to produce hydrogen. The latter was passed through the solution for three hours after which the adsorption bulb was sealed off in a hydrogen atmosphere in *c* and shaken during an hour. Three hours of passing hydrogen and one hour of shaking were quite sufficient for establishing the adsorption equilibrium; then the solution was filtered off from the charcoal by means of a glass filter, *d*, to a bulb, *e*, which was then cut off from the apparatus. The amount of adsorbed cation on the charcoal was determined by volumetric titration of the solution previous and subsequent to the adsorption. As indicator phenol red was used. When titrating easily hydrolized salts a mixture of methyl orange with fluorescein was used as indicator[2]. The experiments were carried out with charcoals of different activity. They were obtained by burning 21, 51 and 88 per cent. of the charcoal during activation. In the following pages these samples of charcoal will be designated as *A*, *B* and *C*. All of them contained 0.2 per cent Pt.

These experiments have shown that charcoal *A* adsorbs univalent cations (Li, Na, K) better than bivalent ones (Ba). The adsorption of tervalent (La) and quadrivalent cations practically does not occur. The result of experiments with charcoal *A* are given in Table 1 (the adsorbed quantities are expressed in milli-equivalents per 1 gr. of charcoal).

In Fig. 2 is shown the relation between the adsorption of cations on charcoal *A* and the logarithm of salt concentration

Table 1

Adsorption on charcoal *A*

c	0.01	0.05	0.1	0.5	1 *N*
LiCl . .	0.012	0.042	0.057	—	0.100
NaCl . .	0.016	0.048	0.062	—	0.107
KCl . .	0.021	0.053	0.072	0.103	0.110
CsCl . .	0.028	0.079	0.107	—	—
$BaCl_2$ . .	0.008	0.017	0.017	0.017	0.017
$LaCl_3$ . .	—	—	0	0.002	—
$ThCl_4$ . .	—	—	0	—	—

[2] Burtstein, Acta Physicochimica URSS, **7**, 311 (1937).

A quite different picture is obtained with charcoal *B*. The adsorption of univalent cations on this charcoal is somewhat larger than that on charcoal *A*, the difference in the amounts adsorbed being

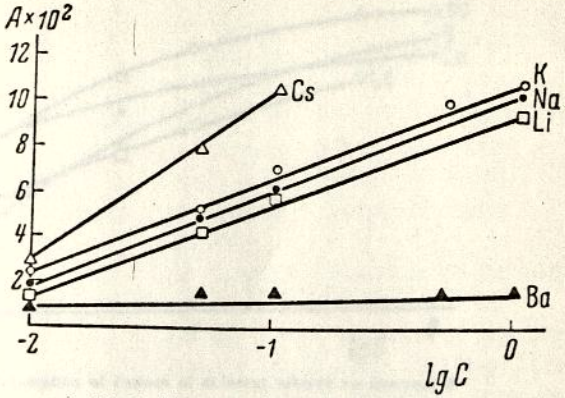

Fig. 2. Adsorption of cations on charcoal *A*.

particularly marked at low concentrations: *e. g.*, at a concentration of 0.01 *N*. The adsorption of the K-ions increases 1.5—2 times. The adsorption of barium on charcoal *B* increases about 8 times

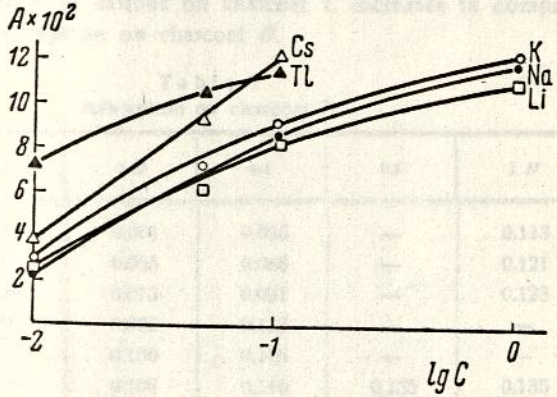

Fig. 3. Adsorption of univalent cations on charcoal *B*.

when compared to the adsorption of barium on charcoal *A*, and exceeds the adsorption of univalent cations. The adsorption of $La^{\cdots}$ from solutions of low concentrations is greater than that of $Ba^{\cdot\cdot}$,

however, with an increase of the concentration, the adsorption of $La^{...}$ becomes less than that of $Ba^{..}$ and $K^{.}$.

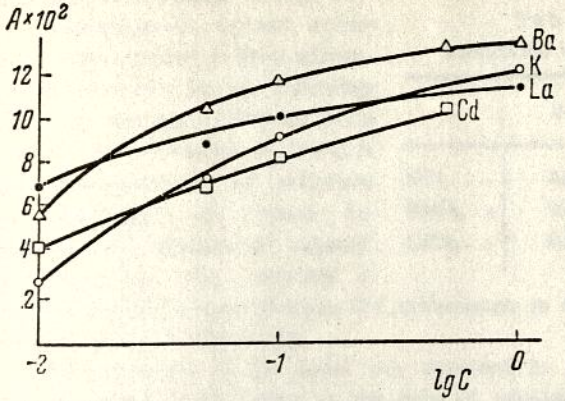

Fig. 4. Adsorption of cations of different valency on charcoal *B*.

The results of experiments with charcoal *B* are shown in Table 2 and in Figs. 3 and 4.

In Fig. 3 is shown the relation between the adsorption of univalent cations on charcoal *B* and the logarithm of concentration.

The adsorption of cations on charcoal *C* increases in comparison with the adsorption on charcoal *B*.

Table 2
Adsorption on charcoal *B*

c	0.01	0.05	0.1	0.5	1 *N*
LiCl . .	0.025	0.064	0.085	—	0.113
NaCl . .	0.024	0.065	0.086	—	0.121
KCl . .	0.029	0.073	0.091	—	0.123
CsCl . .	0.036	0.092	0.122	—	—
$TlNO_3$.	0.071	0.106	0.116	—	—
$BaCl_2$.	0.058	0.106	0.116	0.135	0.135
$CdCl_2$.	0.041	0.070	0.084	0.106	—
$LaCl_3$ . .	0.068	0.088	0.103	—	0.114
$ThCl_4$.	—	—	0.108	—	—

The relation between the adsorption of ions of different valency and the percentage of charcoal burned during the activation process is shown in Fig. 5.

Arranging the cations according to the amount of their adsorption on charcoal *A*, the following series is obtained: K > Ba > La and Th. For charcoals *B* and *C* at low concentrations of solutions the adsorption of cations increases with increase of valency: K < Ba < La. On charcoal *C* at high solution concentrations the differences in the adsorption of cations become very small.

Table 3

Adsorption on charcoal *C*

c	0.01	1 *N*
KCl . .	0.049	0.126
$BaCl_2$. .	0.076	0.136
$LaCl_3$ . .	0.102	0.131

No adsorption of the anion was observed in our experiments. This was particularly tested in the case of solutions of $BaCl_2$ and $ThCl_4$: the concentration of chlorine remained unchanged during the adsorption process.

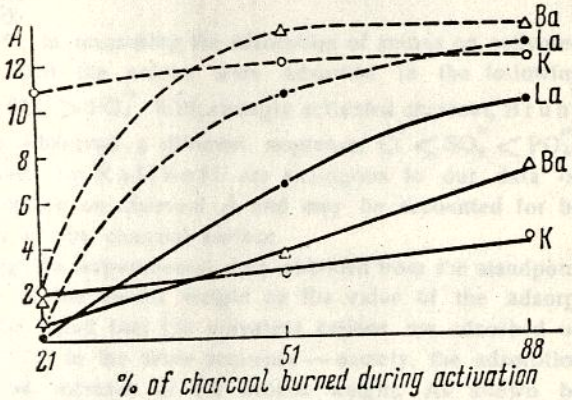

Fig. 5. Relation between the adsorption of cations and the activity of the charcoal. Dotted curves — 1 *N* solutions; solid curves — 0,01 *N* solutions.

Discussion of results

From the standpoint of the electrochemical theory of electrolyte adsorption, the amount of adsorbed cations must increase as the valency of the cation increases. According to the data published

by a number of authors[3], slightly activated charcoal possesses a large inner surface but very narrow pores. In the case of adsorption of organic acids on such charcoal the inversion of Traube's rule is observed ("ultraporosity" effect). On a more prolonged activation, an increase of the pores takes place. In the case of adsorption from solutions the narrow pores of the charcoal are little accessible to large molecules of the substance adsorbed, while for the same particles when adsorbed on strongly activated charcoal having large pores such difficulties do not exist. In our case, when adsorption of cations occurs, their actual sizes in solution may strongly differ from each other owing to the different degrees of hydration.

Univalent cations which possess a relatively small hydration shell can penetrate even into the narrow pores of charcoal of low activity, while bivalent cations like $Ba^{\cdot\cdot}$, and so much the more tervalent ones like $La^{\cdot\cdot\cdot}$, possessing a large hydration shell, are not capable of penetrating into narrow pores and consequently are little adsorbed. On highly activated charcoal having pores with a large diameter, the adsorption of ions with a large hydration shell increases sharply.

Kolthoff[4], in measuring the adsorption of anions on activated charcoal, found that the anions were adsorbed in the following sequence: $Cl' > SO_4'' > PO_4'''$. With strongly activated charcoal, Bruns and Frumkin observed a different sequence: $Cl' < SO_4'' < PO_4'''$. Observations made by Kolthoff are analogous to our data on the cation adsorption on charcoal *A* and may be accounted for by the ultraporosity of the charcoal surface.

In analyzing the experimental data obtained from the standpoint of the influence of the atomic weight on the value of the adsorption it should be noted that the univalent cations are adsorbed on charcoals *A* and *B* in the same sequence — namely, the adsorption increases with an increase of the atomic weight. As shown by Figs. 2 and 3, the difference in the values of the adsorption for lithium, sodium and potassium is small. The adsorption of thallium and caesium considerably increases as compared to the above-mentioned univalent cations. It should be noted that the adsorption iso-

[3] Bruns a. Zarubina, Koll. Z., **64**, 279 (1933). Dubinin a. Zaverina, Acta Physicochimica URSS, **4**, 647 (1936).

[4] Kolthoff, Rec. Trav. Chim. Pays-Bas, **46**, 549 (1927).

therms for the majority of univalent cations studied have a steeper course than those for bivalent and so much the more for tervalent cations. In all the cases considered the adsorption of cations has an electrostatic origin and is caused by the formation of a double electric layer at the charcoal-solution interface as no adsorption of the anion is observed. We have made attempts to calculate the adsorption values for cations of different valence using the double layer theory of Stern[5] and to compare the calculated data with the experimental ones. The calculation was made without taking into consideration the specific adsorption. The capacity of the double layer on the charcoal surface was assumed to be equal to the capacity for mercury (19 μF per cm.^{2}). The surface of 1 gr. of charcoal was assumed to be equal to 500 m.^{2}. The total charge of the external part of the double layer is equal to

$$\varepsilon_0 = \varepsilon_1 + \varepsilon_2 = -F\delta\left(c_1 e^{-\frac{\zeta F}{RT}} + c_2 e^{-\frac{\nu\zeta F}{RT}} - c_3 e^{\frac{\zeta F}{RT}}\right) -$$

$$-\sqrt{\frac{RTD}{2\pi}}\sqrt{c_1\left(e^{-\frac{\zeta F}{RT}}-1\right)+c_2\left(e^{-\frac{\nu\zeta F}{RT}}-1\right)+c_3\left(e^{\frac{\zeta F}{RT}}-1\right)},$$

where c_1, c_2 and c_3 are concentrations of the hydrogen ion, the cation and the anion respectively, D — the dielectric constant, ν — the valence or the cation, ζ — the potential of the diffuse part of the double layer, F — the Faraday number and δ — the thickness of the Helmholtz layer ($\delta = 3.1 \times 10^{-8}$).

The calculation of the potential was made using the method described by Frumkin[6]. The potential difference between the charcoal and the solution, the pH of which is 2, was assumed to be equal to 0.089, since the zero point for charcoal[7] corresponds to a potential of about — 0.027.

Since in the case of adsorption from a solution containing a mixture of electrolytes the calculation of the part of the charge of the diffuse double layer carried by each ion presents considerable difficulties, we used an approximation method of calculation

[5] Stern, Z. Elektrochem., **30**, 508 (1924).
[6] Frumkin, Z. physik. Chem., **164**, 121 (1933).
[7] Bruns, Burstein, Fedotov a. Liwschitz, Acta Physicochimica URSS, **8**, 47 (1938).

assuming an equal distribution of the charge between different ions in the Helmholtz and the diffuse double layers.

In this case the charge produced by the adsorption of the cations of the salt is equal to

$$\varepsilon_k = \varepsilon_0 \frac{c_2 e^{-\frac{\nu_2 F}{RT}}}{c_1 e^{-\frac{\nu_1 F}{RT}} + c_2 e^{-\frac{\nu_2 F}{RT}} - c_3 e^{\frac{\nu_3 F}{RT}}}$$

or, for the adsorption, we obtain the expression: $\Gamma = \frac{\varepsilon_k \times S}{F}$.

The values of the adsorption of cations from solutions of different concentrations of KCl, $BaCl_2$ and $LaCl_3$ thus calculated are given in Table 5. The calculated data were compared with the results for charcoal *B*.

Table 5

c	KCl			$BaCl_2$			$LaCl_3$		
	$\Gamma_{obs.}$	$-\zeta$	$\Gamma_{calc.}$	$\Gamma_{obs.}$	$-\zeta$	$\Gamma_{calc.}$	$\Gamma_{obs.}$	$-\zeta$	$\Gamma_{calc.}$
0.01	0.029	0.0275	0.031	0.058	0.035	0.046	0.068	0.0183	0.057
0.05	0.073	0.0175	0.073	0.106	0.014	0.083	0.088	0.0118	0.098
0.1	0.091	0.0129	0.098	0.116	0.010	0.105	0.103	0.010	0.107

As shown in Table 5, the values obtained for the adsorption of cations according to Stern's theory are in satisfactory agreement with experimental data.

Summary

The adsorption of uni-, bi-, ter- and quadrivalent cations on platinized charcoal in an atmosphere of hydrogen has been measured. It is shown that on highly activated charcoal the cations are adsorbed in the following sequence: $K^{\cdot} < Ba^{\cdot\cdot} < La^{\cdot\cdot\cdot}$, while in slightly activated charcoal the following order is observed: $K^{\cdot} > Ba^{\cdot\cdot} > La^{\cdot\cdot\cdot}$. The inversion of the adsorption sequence was explained by an ultraporosity effect. The results obtained are compared with adsorption data calculated according to Stern's theory.

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The Karpov Institute of Physical Chemistry,
Laboratory of Surface Phenomena, Moscow.

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