# *Adsorption of Ions by Carborundum.*

By G. A. H. Elton and J. W. Mitchell.

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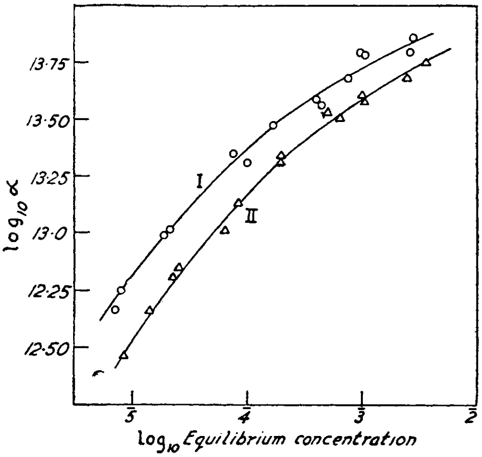
Measurements of the extent of ion adsorption by carborundum from some dilute electrolyte solutions have been made conductometrically, and the results have been used to calculate the energies of adsorption of the individual ions.

Benton and Elton (*Trans. Faraday Soc.*, 1953, **49**, 1213) have shown that for a non-ionogenic surface it is possible to use the results of measurements of adsorption from electrolyte solutions to calculate the energies of adsorption of individual ions, provided that the appropriate electrokinetic charges and potentials are known. This paper gives the results of measurements of adsorption by carborundum, the conductance-loss method described by Benton and Elton (*loc. cit.*) being used, and the calculated adsorption energies for six univalent ions.



I, HCl.
II, $HNO_3$

Solutions of hydrochloric and nitric acids undergo a marked decrease in conductivity on equilibration with a large area of carborundum. The figure shows the values of $\log_{10} \alpha$, the number of solute ions in excess per square cm. in the whole double layer, for these solutions. The number, $n_i^{\mathrm{D}}$, of ions of type $i$ in excess in the diffuse part of the layer can be calculated from the equilibrium bulk concentrations ($n_i^{\mathrm{B}}$ ions per ml.) and the corresponding electrokinetic potential $\zeta$, Grahame's equation (*Chem. Reviews*, 1947, **41**, 441) being used, *viz.*,

$$n_i^{\mathrm{D}} = -2\,\lambda n_i^{\mathrm{B}}[1 - \exp(-z_i e\zeta/kT)] \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $\lambda$ is the Debye–Huckel expression for the effective double layer thickness, $z_i$ is the number of electronic charges, $e$, carried by the ion of type $i$, $k$ is the Boltzmann constant, and $T$ is the absolute temperature. The number of solute ions of each type in the diffuse layer was calculated by using values of $\zeta$ given by Elton and Mitchell (*J.*, 1953, 3690). The corresponding number in the fixed layer, $n_i^{\mathrm{F}}$, was then obtained from the equation

$$n_i^{\mathrm{F}} = \alpha_i - n_i^{\mathrm{D}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

As shown by Benton and Elton (*loc. cit.*), the values of $n_{\mathrm{anion}}^{\mathrm{F}}$ obtained in this way are final, but the values of $n_{\mathrm{H}}^{\mathrm{F}}$ represent only first approximations to the number of adsorbed hydrogen ions, since the conductometric method does not directly detect adsorption of ions produced by the dissociation of the solvent, and the fixed layer will contain an initially unknown number of hydroxyl ions, and an equal additional number of hydrogen ions.

The energy of adsorption per g.-ion of a species of type $i$ is given by

$$E_i = \boldsymbol{R}T \log_e n_i^F/n_i^B + z_i\boldsymbol{F}\zeta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $\boldsymbol{F}$ is the Faraday equivalent. The values of the adsorption energies of the chloride and nitrate ions, together with the first-approximation values for the hydrogen ion, calculated in this way, are given in Table 1.

TABLE 1. *Adsorption energies (in kcal.), from results in acid solutions.*

| Normality | $E_H$* | $E_{Cl}$ | $E_H$* | $E_{NO_3}$ | Normality | $E_H$* | $E_{Cl}$ | $E_H$* | $E_{NO_3}$ |
|---|---|---|---|---|---|---|---|---|---|
| $1 \times 10^{-5}$ | $-6 \cdot 8$ | $-1 \cdot 44$ | $-6 \cdot 9$ | $-1 \cdot 95$ | $2 \times 10^{-4}$ | $-7 \cdot 0$ | $-2 \cdot 81$ | $-7 \cdot 0$ | $-3 \cdot 07$ |
| $2 \times 10^{-5}$ | $-6 \cdot 7$ | $-1 \cdot 66$ | $-6 \cdot 8$ | $-2 \cdot 05$ | $5 \times 10^{-4}$ | $-7 \cdot 2$ | $-3 \cdot 39$ | $-7 \cdot 2$ | $-3 \cdot 57$ |
| $5 \times 10^{-5}$ | $-6 \cdot 8$ | $-2 \cdot 01$ | $-6 \cdot 9$ | $-2 \cdot 40$ | $1 \times 10^{-3}$ | $-7 \cdot 3$ | $-3 \cdot 83$ | $-7 \cdot 4$ | $-3 \cdot 96$ |
| $1 \times 10^{-4}$ | $-6 \cdot 9$ | $-2 \cdot 40$ | $-6 \cdot 9$ | $-2 \cdot 71$ | $2 \times 10^{-3}$ | $-7 \cdot 7$ | $-4 \cdot 29$ | $-7 \cdot 6$ | $-3 \cdot 29$ |

* First approximation only.

Solutions of potassium chloride, potassium nitrate, and sodium chloride show an increase in conductivity on equilibration with a large area of carborundum. However, the electrokinetic charge is greater in these solutions than in the acid solutions (Elton and Mitchell, *loc. cit.*), so that considerable adsorption must in fact occur. The rise in conductivity was attributed to the fact that hydrogen ions are released from the diffuse layer, owing to the decrease in electrokinetic potential caused by the presence of the salt; since the mobility of the hydrogen ion is much greater than that of any of the solute ions in the salt solutions, the release of a relatively small number of hydrogen ions could produce an increase in conductivity greater than the decrease caused by the adsorption of solute ions. On this basis, using the values for the adsorption energies of the solute anions at the appropriate concentrations, obtained from the work on acid solutions, we can calculate the numbers of ions of each type adsorbed into the fixed layer, Benton and Elton's (*loc. cit.*) method of successive approximations being used. The values for the adsorption energy of the hydrogen ion used in this calculation are the first-approximation values obtained as described above. The adsorption energies for the sodium and potassium ions, obtained in this way, are given in Table 2.

TABLE 2. *Adsorption energies (in kcal.), from results in salt solutions.*

| Normality | $E_K$(KCl) | $E_K$($KNO_3$) | $E_{Na}$(NaCl) | Normality | $E_K$(KCl) | $E_K$($KNO_3$) | $E_{Na}$(NaCl) |
|---|---|---|---|---|---|---|---|
| $1 \times 10^{-5}$ | $-6 \cdot 4$ | $-6 \cdot 4$ | $-6 \cdot 5$ | $2 \times 10^{-4}$ | $-6 \cdot 9$ | $-6 \cdot 9$ | $-6 \cdot 8$ |
| $2 \times 10^{-5}$ | $-6 \cdot 6$ | $-6 \cdot 6$ | $-6 \cdot 4$ | $5 \times 10^{-4}$ | $-7 \cdot 1$ | $-7 \cdot 1$ | $-7 \cdot 0$ |
| $5 \times 10^{-5}$ | $-6 \cdot 6$ | $-6 \cdot 6$ | $-6 \cdot 5$ | $1 \times 10^{-3}$ | $-7 \cdot 3$ | $-7 \cdot 2$ | $-7 \cdot 2$ |
| $1 \times 10^{-4}$ | $-6 \cdot 8$ | $-6 \cdot 7$ | $-6 \cdot 6$ | $2 \times 10^{-3}$ | $-7 \cdot 4$ | $-7 \cdot 5$ | $-7 \cdot 4$ |

Elton and Mitchell (*loc. cit.*) have shown that the electrokinetic charge on a carborundum surface in water of high purity is very small, and tends towards zero as the amount of electrolyte impurities in the water is reduced. It therefore appears reasonable to assume that carborundum takes up its charge entirely by ion adsorption, and not by surface ionisation, *i.e.*, we may write

$$\sigma_1 = -\sigma_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $\sigma_1$ is the charge in the fixed layer, and $\sigma_2$ that in the diffuse layer, measured in electrokinetic experiments. Furthermore

$$\Sigma z_i e n_i^F = \sigma_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

It is found that in order to satisfy equation (5), it is necessary to assume the adsorption of a fairly large number of anions from the solvent. Assuming (see Benton and Elton, *loc. cit.*) that all of the anions adsorbed from conductivity water are hydroxyl ions (*i.e.*, neglecting bicarbonate and other ions), we can obtain $n_{OH}^F$ from equation (5), and hence, using equation (3), obtain a value of $E_{OH}$. This value will be only a first approximation, in view of the use of the approximate value of $E_H$. The hydroxyl-ion concentrations in the salt solutions are similar to those in the more dilute acid solutions, and the first-approximation values of $E_{OH}$ interpolated at appropriate concentrations may be used to obtain first estimates of $n^F_{OH}$ in the most dilute acid solutions. Hence we obtain second-approximation values of $n^F_H$, given by

$$(n^F_H)_2 = (n^F_H)_1 + (n^F_{OH})_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $(n^F_H)_1$ and $(n^F_H)_2$ are respectively the first and second approximations to $n^F_H$, and $(n^F_{OH})_1$ is the first approximation to $n^F_{OH}$. $(n^F_H)_2$ may then be used in equation (3) to obtain a second approximation to $E_H$, which can be used in turn in the calculation for the salt solutions. The system of successive approximations is continued until constant values of $E_H$ and $E_{OH}$ are obtained. It may be noted that the calculated values of the adsorption energies of the cation and anion from the salt are not affected in this process.

Tables 3 and 4 summarise the results obtained for the salt solutions and for the more dilute acid solutions. It is not possible to perform the complete calculation indicated above for acid solutions of concentrations of 1 × $10^{-4}$N and above, for the values of $n^B_{OH}$ in these solutions are lower than those obtained in any of the salt solutions. However, as the acid concentration rises, $n^F_{OH}$ falls, and eventually will become negligible with respect to $n^F_H$, in which case the first-approximation value of $E_H$ will be equal to the final value. In order to obtain the final interpolated values of $E_H$ given in Table 5, we have assumed that this is the case in the most concentrated acid solutions studied, *viz.*, 2 × $10^{-3}$N. It is possible, therefore, that the value of —7·6 kcal. taken at this concentration is slightly low (too negative), but it is considered unlikely that hydroxyl-ion adsorption is at all significant at such concentrations.

TABLE 3. *Final results for dilute acid solutions.*

| Normality | Acid | $n^F_H \times 10^{-13}$, ions/cm.$^2$ | $n^F_{OH} \times 10^{-13}$, ions/cm.$^2$ | $E_H$, kcal. | $E_{OH}$, kcal. |
|---|---|---|---|---|---|
| $1 \times 10^{-5}$ | HCl (1) | 2·2 | 1·7 | −5·9 | 4·8 |
| | HCl (2) | 1·5 | 1·0 | −6·2 | 4·5 |
| | $HNO_3$ | 1·2 | 0·9 | −6·1 | 4·3 |
| $2 \times 10^{-5}$ | HCl (1) | 2·5 | 1·6 | −6·1 | 5·1 |
| | HCl (2) | 2·0 | 1·1 | −6·3 | 4·8 |
| | $HNO_3$ | 1·7 | 1·1 | −6·3 | 4·7 |
| $5 \times 10^{-5}$ | HCl (1) | 2·5 | 0·9 | −6·6 | 5·1 |
| | HCl (2) | 2·2 | 0·6 | −6·6 | 4·9 |
| | $HNO_3$ | 2·5 | 0·8 | −6·4 | 5·2 |

HCl (1), from combination of results for HCl and KCl.
HCl (2), from combination of results for HCl and NaCl.
$HNO_3$, from combination of results for $HNO_3$ and $KNO_3$.

TABLE 4. *Final results for salt solutions.*

| Normality | Salt | $n^F_{OH} \times 10^{-13}$, ions/cm.$^2$ | $n^F_H \times 10^{-13}$, ions/cm.$^2$ | $E_H$, kcal. | $E_{OH}$, kcal. |
|---|---|---|---|---|---|
| $2 \times 10^{-5}$ | KCl | 1·5 | 1·8 | −5·9 | 4·5 |
| | NaCl | 1·0 | 1·2 | −6·1 | 4·4 |
| | $KNO_3$ | 1·1 | 1·1 | −6·0 | 4·2 |
| $2 \times 10^{-4}$ | KCl | 1·4 | 2·8 | −6·2 | 5·1 |
| | NaCl | 1·1 | 2·1 | −6·3 | 4·9 |
| | $KNO_3$ | 1·0 | 1·9 | −6·3 | 4·7 |
| $2 \times 10^{-3}$ | KCl | 0·7 | 3·6 | −6·4 | 5·1 |
| | NaCl | 0·7 | 2·6 | −6·4 | 4·9 |
| | $KNO_3$ | 0·8 | 3·5 | −6·5 | 5·2 |

TABLE 5. *Adsorption energy of the hydrogen ion (final values).*

| Normality | $1 \times 10^{-5}$ | $2 \times 10^{-5}$ | $5 \times 10^{-5}$ | $1 \times 10^{-4}$ | $2 \times 10^{-4}$ | $5 \times 10^{-4}$ | $1 \times 10^{-3}$ | $2 \times 10^{-3}$ |
|---|---|---|---|---|---|---|---|---|
| $E_H$, kcal. | −6·1 | −6·2 | −6·5 | −6·7 | −6·9 | −7·2 | −7·4 | −7·6 |

As seen from Table 2, the values of $E_K$ obtained from potassium chloride and from potassium nitrate are in agreement to ±0·1 kcal. over the whole concentration range. The agreement between values of $E_H$ calculated from different systems is slightly less close, but is very satisfactory, bearing in mind the assumptions involved, and the indirect method of calculation necessary. There is little difference between the energies for sodium and potassium ions, $E_{\text{Na}}$ being generally slightly higher (more positive). The energies for these ions, and for the hydrogen ion, are roughly 1 kcal. higher for carborundum than for silica (Benton and Elton, *loc. cit.*). $E_{\text{Cl}}$ and $E_{\text{NO}_3}$ for carborundum are very similar to the corresponding values for silica, and it is possible that for these ions, adsorption on the two solids occurs on sites of similar type.

## EXPERIMENTAL

100-Mesh carborundum powder, supplied by the Carborundum Co., Ltd., was cleaned as described by Elton and Mitchell (*loc. cit.*), and freed from any fine material by washing and decantation. The surface area per g. ($1{\cdot}01 \times 10^3$ cm.$^2$) was determined, and the electrolytes used were purified, by the methods of Dulin and Elton (*J.*, 1952, 286). Conductivity water was prepared by the ion-exchange method; its conductivity was usually 0·2—0·3 gemmho, and was always less than 0·5 gemmho. Benton and Elton (*J.*, 1953, 2096) have shown that water so prepared is suitable for use in electrokinetic experiments.

Apparatus and experimental technique were as described by Benton and Elton (*Trans. Faraday Soc.*, *loc. cit.*). Addition of carborundum to water was found to produce a rise in conductivity, proportional to the area/volume ratio ($\theta$), and equal to $2{\cdot}0 \times 10^{-9}$ ohm$^{-1}$ cm.$^{-1}$ $\theta^{-1}$; this was ascribed to the dissolution of a surface layer on the carborundum (cf. a similar effect for silica), giving colloidal particles with hydrogen gegen-ions. Blank conductivity runs in water previously equilibrated with a large area of carborundum showed that the conductivity of the dissolved material was additive to that of dissolved acids and salts, but was largely suppressed by dissolved alkali.

All experiments were carried out at 25·00° ± 0·01°.

BATTERSEA POLYTECHNIC, LONDON, S.W.11

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