EFFECT OF HALIDES ON THE REACTION OF ALUMINIUM SINGLE CRYSTAL IN AQUEOUS SODIUM HYDROXIDE

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The effect of sodium halides on the reaction rate and potential of an aluminium single crystal in aqueous solution of NaOH is studied. Fluoride, bromide and iodide ions exert an inhibiting effect, which is explained in terms of their specific adsorption on the solid surface, whereas chloride ions have a stimulating effect on the reaction rate, presumably due to the formation of complex surface intermediates.

The effect of halides on the reaction of aluminium in aggressive media is related to their specific adsorption on the surface of the metal or on the oxide layer, activating dissolution of the latter[1-6]. Thus, dependent on the reaction mechanism involved, the effect of halides on the reaction of aluminium can be different in strongly acid and strongly basic solutions. Based on studies of the mechanisms of reactions of various metals in basic solutions containing alkali halide, some authors (e.g. refs[1,3,4]) suggest that competing with OH^- ions, halide ions participate in the reaction.

In the present work we are concerned with the effect of halides on the reaction rate and potential of an aluminium single crystal in aqueous NaOH; the experimental data are interpreted in terms of the reaction mechanism suggested previously[7,8].

EXPERIMENTAL

The experimental arrangement and methodology of the kinetic and potential measurements were as in refs[7,8]. The Al $\{100\}$ and $\{111\}$ planes were subject to examination, the solution contained NaOH in a concentration of 1 mol dm^{-3} and NaF, NaCl, NaBr or NaI in variable concentrations; temperature of measurement was $25.0 \pm 0.1°C$. In solutions containing NaF, dissolved aluminium was determined following ref.[9].

Chemicals used were of reagent grade purity. Reproducibility of kinetic measurements was $\pm 3\%$, reproducibility of steady-state potential values was ± 3 mV.

RESULTS AND DISCUSSION

The time dependences of the amount of dissolved aluminium in the solution were invariably linear for the two planes. Both the reaction rate and the steady-state

potential were unaffected by addition of halides at concentrations of 10^{-7} to 10^{-4} mol dm^{-3}.

The time dependences of the aluminium potential during the reaction were non-linear; some are shown in Fig. 1 for the $\{111\}$ plane. The dependences of the rate of dissolution of Al and of the steady-state potential on the concentration of halide are shown in Figs 2−5 for the two planes studied. The following facts are demonstrated:

a) Sodium fluoride has an inhibiting effect on the reaction of the two aluminium crystal planes at concentrations exceeding 10^{-3} mol dm^{-3}. This inhibiting effect increases with increasing concentration of NaF, and the steady-state potential shifts to more negative values (Fig. 2). The parallel shape of the concentration dependences of the reaction rate and the steady-state potentials at the planes studied is of interest.

b) Sodium bromide and iodide also exert an inhibiting effect on the reaction of the two aluminium planes (Figs 3, 4), the dependences of the steady-state potentials of Al $\{100\}$ and Al $\{111\}$, however, merge at NaBr or NaI concentrations in excess of 0·1 mol dm^{-3}.

c) The effect of sodium chloride is substantially different from that of the remaining halides (Fig. 5). At NaCl concentrations higher than 10^{-2} mol dm^{-3}, a slight stimulating effect was observed at approximately 0·3 and 0·5 mol dm^{-3} for Al $\{111\}$ and Al $\{100\}$, respectively. At NaCl concentrations higher than as corresponds to the maximum reaction rate, the steady-state potential shifts somewhat to more negative values.
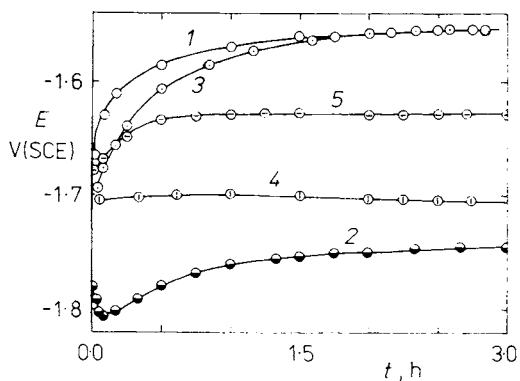

FIG. 1

Time course of potential of the Al $\{111\}$ plane in 1M-NaOH in the absence of halide (*1*) and in the presence of halide at a concentration of 0·5 mol dm^{-3} (*2*−*5*). Halide: *2* NaF, *3* NaCl, *4* NaBr, *5* NaI

In accordance with the concept suggested previously[8], these facts can be so explained that in competition with the OH^- ions, the halide ions are specifically
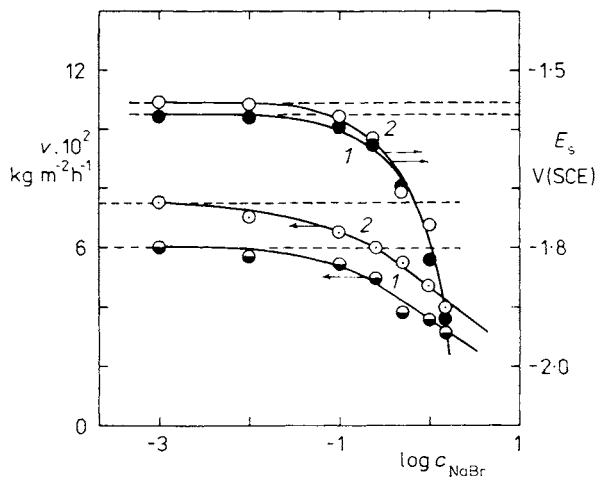
FIG. 2

Effect of NaF (log c_{NaF}) on the reaction rate v and steady-state potential E of aluminium crystal planes; values in pure 1M-NaOH are indicated by dashed lines. Plane: 1 $\{100\}$, 2 $\{111\}$
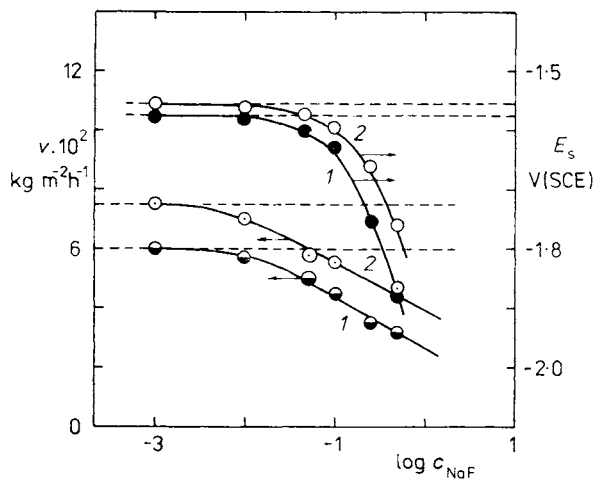
FIG. 3

Effect of NaBr (log c_{NaBr}) on the reaction rate v and steady-state potential E of aluminium crystal planes. Plane: 1 $\{100\}$, 2 $\{111\}$

adsorbed on the metal surface or take part in the process of formation of complex surface intermediates. This is borne out by the shift of the steady-state potential to
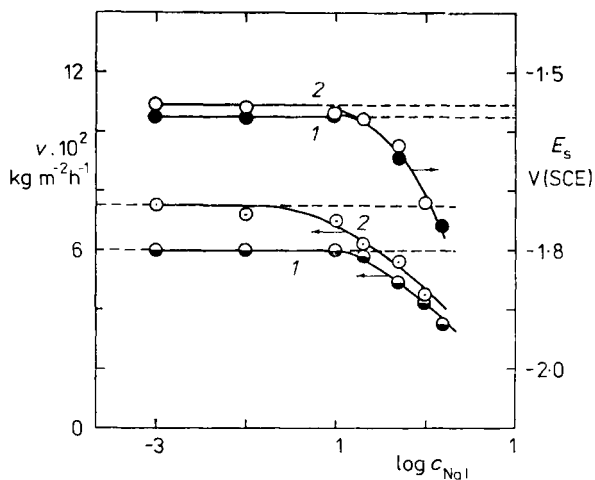

FIG. 4

Effect of NaI (log c_{NaI}) on the reaction rate v and steady-state potential E of aluminium crystal planes. Plane: 1 $\{100\}$, 2 $\{111\}$
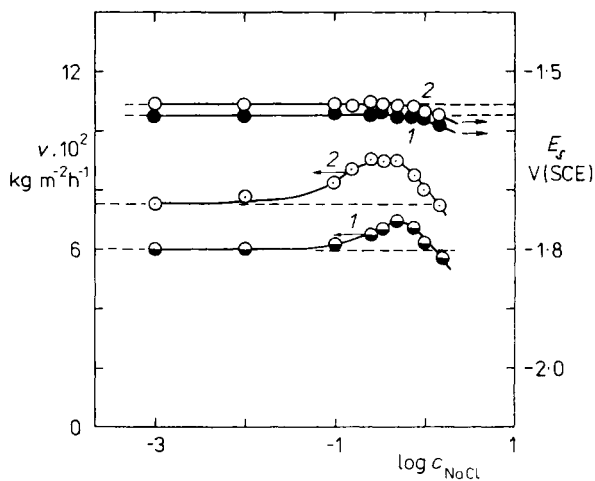

FIG. 5

Effect of NaCl (log c_{NaCl}) on the reaction rate v and steady-state potential E of aluminium crystal planes. Plane: 1 $\{100\}$, 2 $\{111\}$

more negative values with increasing concentration of halide. The presence of halide ions on the surface of the reacting aluminium is also evidenced by the initial potential values (Fig. 1); at halide concentrations at which their effect on the reaction rate was evident, the initial potentials at the two planes were more negative than at lower concentrations where the halides had no effect on the reaction.

Based on the dependences shown in Figs 2—5, halides can be divided into two groups with respect to their effect on the reaction of aluminium in NaOH solutions, viz. halides exerting an inhibiting effect (fluoride, bromide, iodide) and those exerting an activating effect (chloride).

For the former, their effect on the reaction can be expressed in terms of the effective degree of coverage Θ of the aluminium surface,

$$\Theta = 1 - v/v_0 , \qquad (1)$$

where v and v_0 are the reaction rates in the presence and absence of halide, respectively.

We described the adsorption by the simplified Temkin isotherm

$$\Theta = 2 \cdot 3RT \log (\beta c)/\alpha , \qquad (2)$$

where c is the molar concentration of halide in solution, α is the interaction coefficient, β is the adsorption coefficient of the halide ions, R is the molar gas constant and T is the thermodynamic temperature. The dependences of the degree of coverage Θ on the logarithm of halide concentration are shown in Figs 6—8 for the three inhibiting halides respectively, The calculated α and β values for the Al $\{100\}$ and Al $\{111\}$ planes are given in Table I.

TABLE I
Coefficients α and β and standard deviation σ in Eq. (2)

Ion adsorbed	α kJ mol^{-1}		β mol^{-1}		σ	
	Al $\{100\}$	Al $\{111\}$	Al $\{100\}$	Al $\{111\}$	Al $\{100\}$	Al $\{111\}$
F$^-$	22·09	31·87	121·75	284·20	0·03	0·02
Br$^-$	17·50	20·63	18·41	24·15	0·04	0·03
I$^-$	13·14	18·11	5·69	16·16	0·02	0·03

The high values of the interaction coefficient indicate that the adsorbed halide ions are bonded to the metal surface also by the effect of other species present, viz. (refs[7,8]) the $Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_3$ intermediates.
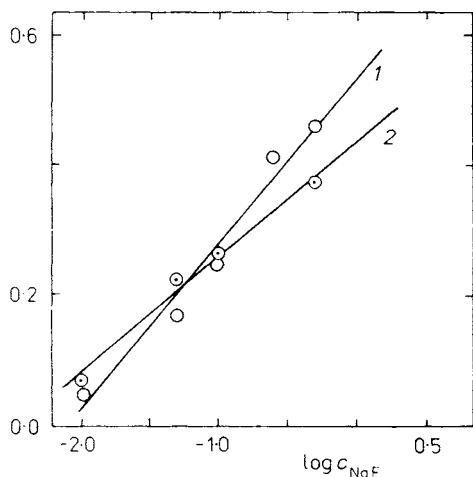
FIG. 6

Dependence of the degree of coverage Θ on the concentration of NaF (log c_{NaF}). Plane: 1 $\{100\}$, 2 $\{111\}$
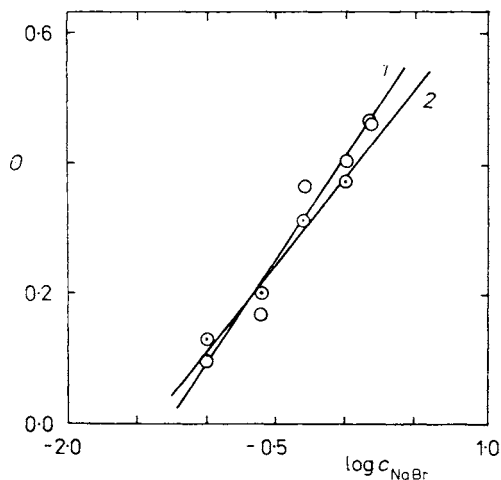
FIG. 7

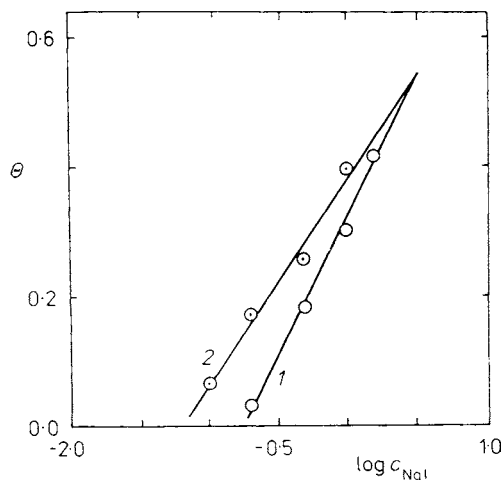Dependence of the degree of coverage Θ on the concentration of NaBr (log c_{NaBr}). Plane: 1 $\{100\}$, 2 $\{111\}$

FIG. 8

Dependence of the degree of coverage Θ on the concentration of NaI (log c_{NaI}). Plane: 1 $\{100\}$, 2 $\{111\}$

The α and β values are higher for the Al $\{111\}$ plane than for the Al $\{100\}$ plane, indicating that the halide ions are adsorbed more strongly on the more reactive plane. Also, on a unit surface area of the more reactive plane there are formed more intermediates strengthening the adsorption bonding of the halide ion to the surface. The α and β coefficients increase in the same order at the two planes, viz. $\alpha_{I^-} < < \alpha_{Br^-} < \alpha_{F^-}$ and $\beta_{I^-} < \beta_{Br^-} \ll \beta_{F^-}$.

The inhibiting effect of halide ions can be explained in terms of their adsorption competition with OH^- ions. The adsorption coefficient values demonstrate that of the halides, fluoride ions are bonded most strongly. This gives rise to the low-soluble AlF_3 and Na_3AlF_6 (ref.[6]), which is apparently related with the minimum in the time course of the potential of Al planes reacting in solutions containing NaF, as well as with the slower potential establishment in such solutions (Fig. 1, curve 2).

The effect of chloride on the reaction under study is qualitatively different from that of the other halides; this is presumably related with the formation of well-soluble complex compounds of the $Al(OH)_xCl_y$ type, as suggested also by the authors[1,10]. Really, hydroxochloride complexes are transformed to the soluble products $Al(OH)_4^-$ and $AlCl_3$ in the hydrated form more rapidly than the hydroxocomplex intermediates, thereby affecting the reaction rate in a positive manner. Increasing concentration of chloride in the solution affects the solubility of the products and the adsorption of OH^- ions, and thus, after surpassing a concentration limit, the stimulating effect is reduced with additional increase in the NaCl concentration.

As compared to the Al $\{100\}$ plane, the stimulating effect of chloride at the more reactive Al $\{111\}$ plane is more marked and its maximum is attained at lower NaCl concentrations; this indicates that at differently reactive planes, chloride ions participate in the complexing reactions to a different extent.

REFERENCES

1. Izotova S. G., Sysoeva V. V., Artyugina E. D.: Zh. Prikl. Khim. *9*, 2115 (1985).
2. Dražić D. M., Začević S. K., Atanasoski R. T., Despić A. R.: Electrochim. Acta *28*, 751 (1983).
3. El-Tantawy Y. A., Al-Kharafi F. M.: Electrochim. Acta *27*, 619 (1982).
4. Iofa Z. A., Rozhdestvenskaya G. B.: Dokl. Akad. Nauk SSSR *91*, 1159 (1953).
5. Kabanov B. N.: *Elektrokhimiya metallov i adsorbtsiya*, p. 161. Nauka, Moscow 1966.
6. Kozin L. F.: *Kinetika i mekhanizm elektrodnykh reaktsii*, p. 128. Nauka Kaz. SSR, Alma-Ata 1980.
7. Miadoková M., Plchová M., Halaša I.: Collect. Czech. Chem. Commun. *52*, 88 (1987).
8. Miadoková M., Šiška J.: Collect. Czech. Chem. Commun. *52*, 1461 (1987).
9. Hofmann P.: *Jednotné metody chemického rozboru vod*, p. 194. Published by SNTL — Nakladatelství technické literatury, Prague 1965.
10. Foley R. T., Nguyen T. H.: J. Electrochem. Soc. *129*, 464 (1982).