STUDY OF THE INFLUENCE OF TETRAALKYLAMMONIUM SALTS ON THE DISSOLUTION OF ALUMINIUM IN AQUEOUS NaOH SOLUTIONS

Milica MIADOKOVÁ, Ivan HALAŠA and Martin KOREŇ

Department of Physical Chemistry, Comenius University, 842 15 Bratislava

Tetraalkylammonium halides decelerate the reaction of aluminium in aqueous NaOH solutions. Their effect depends on the alkyl group, on the anion, and on their concentration; and it is additive with the effect of Ca^{2+} ions. The inhibition effects under study and the shift of the stationary potentials to more anodic values are shown to be related with the influence on the cathodic process, resulting in a retardation of the whole corrosion process.

With regard to reduction of the loss of aluminium during pickling in strongly alkaline media, it is important to find an inhibitor with the highest possible efficiency, which would satisfy the requirements about quality and appearance of the metal surface. Various organic substances are often used as inhibitors, and the donor-acceptor properties of the metal-organic molecule system are evaluated[1,2]; binary systems organic compound-inorganic salt are also sometimes used[3,4]. A survey of the known inhibitors of aluminium corrosion in alkaline media was given by Desai and co-workers[5].

As a continuation of our preceding work[6,7], we turned our attention to ammonium quaternary halides, which have been used in recent years to accelerate phase transition reactions in systems of mutually immiscible liquids[8,9]. These compounds were studied as inhibitors of aluminium corrosion in alkaline medium, but only in the form of polymeric tetraalkylammonium chloride[10,11].

The aim of the present work was to study more closely the action of simple tetraalkylammonium halides on the corrosion of aluminium in alkaline medium.

EXPERIMENTAL

The experiments were carried out in a laboratory flask of 1 dm^3 holding capacity. The temperature was maintained by an ultrathermostat at 25 ± 0.1°C. The reaction solution was stirred with an electromagnetic stirer at 1 000 r.p.m. open to the air.

The aluminium used was of technical grade, its composition was 99.5% Al, 0.26% Fe, 0.13% Si, 0.08% Mg, 0.02% Ti, and 0.01% Cu. The Al samples were prismatic and all faces except for the working face (1 cm^2) were insulated with a CHS EPOXY 1200 resin. The working face was

ground with a metallographic paper (No. 0–6), polished with a deer-skin, and rinsed with ethanol. The samples were activated for 5 min in 20% NaOH solution before use. To ensure equal hydrodynamic conditions during the experiments, the samples were (after rinsing with redistilled water and drying) immersed in the reaction solution 1 cm apart from the stirrer.

The dissolved Al was determined spectrophotometrically[12] by using eriochromcyanin R. The hydrogen evolved was determined volumetrically according to Akimov[13].

The rate of the reaction, $v^{(m)}$, referred to 1 m^2 area, was given by the slope of the linearized dependence of the dissolved quantity on the time (in kg m^{-2} h^{-1}) found in the interval 30 to 90 min. Similarly, the reaction rate $v^{(V)}$ was calculated from the dependence of the volume of evolved hydrogen on the time (in dm^3 m^{-2} h^{-1}). The volume was reduced to standard conditions.

The influence of the studied substances on the reaction was expressed in per cent according to the equation

$$I = 100(v_0 - v)/v_0 ,$$

where v_0 denotes the reaction rate in 1 mol dm^{-3} NaOH and v is the reaction rate in the presence of the additive. Superscripts (m) and (V) are used to denote the technique of measurement. The potential of the Al electrodes was measured by the method described earlier[14] in parallel with the kinetic measurements.

The Ca halides were of reagent grade, the quaternary ammonium halides were pure. Solutions were prepared from redistilled water. The results of kinetic measurements are mean values from three experiments, the reproducibility was about 3–5%. The potential measurements were accurate to within ±0.5 mV and reproducible to ±5 mV.

RESULTS AND DISCUSSION

Influence of the Alkyl Chain of Quaternary Ammonium Salts

To find an optimum salt concentration with regard to highest efficiency and minimum consumption, we measured the dissolution rate at various concentrations of tetra-butylammonium bromide. The inhibition effect was observed in the concentration range from 10^{-4} mol dm^{-3} up to saturation; the concentration dependence resembled a Langmuir isotherm (Fig. 1) similar to that observed earlier[7,15,16]. The limiting inhibition was attained already at a concentration of 10^{-3} mol dm^{-3}.

The reaction was also inhibited by additions of tetramethylammonium bromide $(C_4H_{12}BrN)$, tetraethylammonium bromide $(C_8H_{20}BrN)$, tetrapropylammonium bromide $(C_{12}H_{28}BrN)$, tetrabutylammonium bromide $(C_{16}H_{36}BrN)$, and cetyltrimethylammonium bromide $(C_{19}H_{42}BrN)$ in concentrations of $10^{-3} - 10^{-2}$ mol . . dm^{-3}. The rate of Al dissolution decreased slightly with increasing molecular mass (Table I), and it would probably decrease further if alkyl groups of a still higher molecular mass were used. The negatively charged metal surface is apparently covered with an adsorption layer of quaternary ammonium cations whose stability increases with increasing chain length. For the corrosion process and evolution of hydrogen to proceed, a constant supply of H^+ ions or water molecules to the inter-
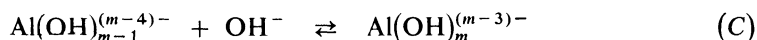
face is needed,

$$H_2O + e^- \rightarrow \tfrac{1}{2} H_2 + OH^- . \qquad\qquad (A)$$

As a result of coulombic repulsion, the adsorbed layer of cations probably retards the transport of hydrogen ions and water dipoles to the interface, whereas the reactants OH^- and products (complex anions) will be transported more quickly as in the case of polymeric ammonium salts[10]. This fact can influence the anodic process

$$Al \rightarrow Al^{3+} + 3 e^- \qquad\qquad (B)$$

involving the steps $(m = 1-4)$[17]

$$Al(OH)_{m-1}^{(m-4)-} + OH^- \rightleftarrows Al(OH)_m^{(m-3)-} \qquad\qquad (C)$$

and it will probably result in a slowing down of the corrosion process.

In the course of the reaction a periodicity was observed, viz., the reaction rate was a function of the time (Fig. 2). This effect disappeared after a sufficiently long time (more than 3 h). We assume that the Al corrosion products form a complex with the quaternary ammonium salt, as in the case of the determination of Al in the presence of dicarboxylic acids[12]. Thus, the concentration of the products determined spectrophotometrically will differ from the true concentration. In the presence of an excess of OH^- ions and Al hydroxo complexes increasing with the time the stability of
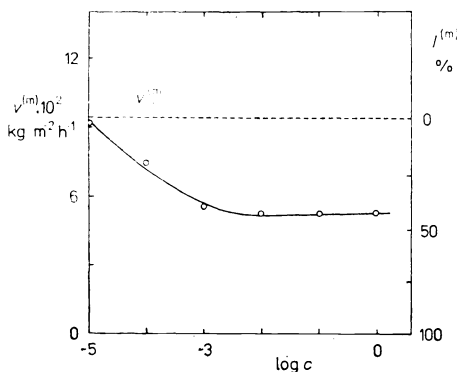

FIG. 1

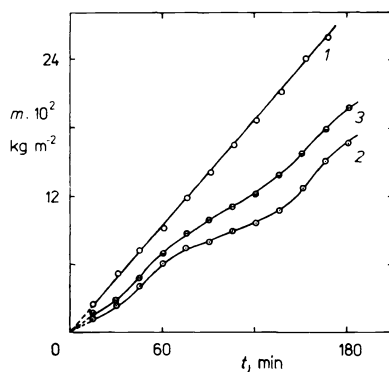Dependence of the dissolution rate of Al in 1 mol dm^{-3} NaOH on the concentration of added $C_{16}H_{36}BrN$

FIG. 2

Typical dependences of the quantity of dissolved Al, m, in 1 mol dm^{-3} NaOH on the time. *1* Non-inhibited system; *2* 10^{-3} mol . . dm^{-3} $C_{16}H_{36}BrN$; *3* 10^{-2} mol dm^{-3} C_4. .$H_{12}BrN$

these complexes is likely to decrease, the quantity of Al that can be determined by the method used increase until a new equilibrium is established and the process can be repeated.

The interpretation based on a limitation of the analytical method is supported by the fact that no periodicity is observed on the dependence of the volume of hydrogen on the time (Fig. 3). The measured values of $v^{(V)}$ did not correspond to $v^{(m)}$ obtained from the linearized dependence of the quantity of dissolved Al on the time according to the equation[17]

$$Al + \tfrac{1}{4} O_2 + OH^- + 2 H_2O \rightleftarrows \tfrac{1}{2} H_2 \qquad (D)$$
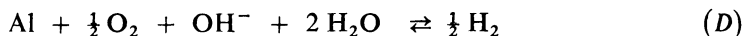
and they were somewhat higher (Table I).

Since the reaction can proceed in the absence of oxygen by the scheme

$$Al + OH^- + 3 H_2O \rightleftarrows [Al(OH)_4]^- + \tfrac{3}{2} H_2 \qquad (E)$$
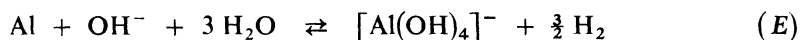
however the values of $v^{(V)}$ are much lower than would correspond to $v^{(m)}$ according to reaction (E), it is obvious that the "mixed" depolarisation process (D) predominates. Eventually, the values of $v^{(V)}$ and $v^{(m)}$ can be correlated after correction for the vapour tension above the NaOH solution[18].
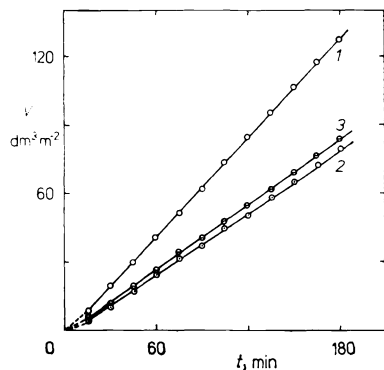

FIG. 3

Typical dependences of the volume of evolved hydrogen, V, on the time in 1 mol dm^{-3} NaOH. *1* No addition; *2* 10^{-3} mol dm^{-3} $C_{16}H_{36}BrN$; *3* 10^{-2} mol dm^{-3} $C_4H_{12}BrN$
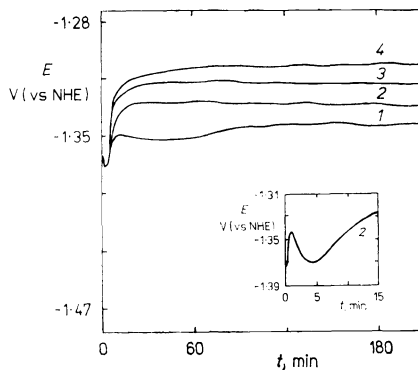

FIG. 4

Typical dependences of the electrode potential of Al on the time in 1 mol dm^{-3} NaOH. *1* No addition; *2* 10^{-3} mol dm^{-3} C_4H_{12}. .BrN; *3* 10^{-3} mol dm^{-3} $C_{16}H_{36}BrN$; *4* 10^{-3} mol dm^{-3} $C_{16}H_{36}BrN + 10^{-4}$ mol . . dm^{-3} Ca^{2+}

Influence of the Quaternary Ammonium Salt Anion

We followed the influence of tetrabutylammonium iodide, bromide, and chloride in concentrations 10^{-3} and 10^{-2} mol dm^{-3} on the studied reaction. The inhibition effects of iodide and bromide were the same within the limits of errors, but the effect of chloride was lower (Table II).

TABLE I

Influence of the alkyl chain of quaternary ammonium bromides on the dissolution rate of Al in NaOH and its stationary potential. $v_0^{(m)} = 0.094$ kg m^{-2} h^{-1}, $v_0^{(V)} = 42.1$ dm^3 m^{-2} h^{-1}, $E_{st} = -1.352$ V, electrolyte 1 mol dm^{-3} NaOH

Quaternary salt	Concentration mol dm^{-3}	$v^{(m)} \cdot 10^2$ kg m^{-2} h^{-1}	$v^{(V)}$ dm^3 m^{-2} h^{-1}	E_{st} V
C$_4$H$_{12}$BrN	10^{-3}	6·5	29·3	−1·328
	10^{-2}	6·3	29·2	−1·317
C$_8$H$_{20}$BrN	10^{-3}	6·3	28·7	−1·326
	10^{-2}	6·3	28·5	−1·314
C$_{12}$H$_{28}$BrN	10^{-3}	5·9	27·6	−1·320
	10^{-2}	6·0	27·3	−1·314
C$_{16}$H$_{36}$BrN	10^{-3}	5·6	26·4	−1·314
	10^{-2}	5·4	26·1	−1·308
C$_{19}$H$_{42}$BrN	10^{-3}	5·5	25·8	−1·315
	10^{-2}	5·4	25·9	−1·306

TABLE II

Influence of the quaternary ammonium salt cation on the dissolution of Al in NaOH

Quaternary salt	Concentration mol dm^{-3}	$I^{(m)}$ %	$I^{(V)}$ %
C$_{16}$H$_{36}$IN	10^{-3}	41·5	38·2
	10^{-2}	40·0	38·5
C$_{16}$H$_{36}$BrN	10^{-3}	40·4	37·3
	10^{-2}	42·6	38·0
C$_{16}$H$_{36}$ClN	10^{-3}	22·3	20·7
	10^{-2}	20·2	21·1

With respect to the electronegativity, size, and deformability of the anions, the lower effect of chloride can be expected. The decrease of the inhibition in the case of chlorides is also in accord with the concept according to which Cl^- ions adsorbed on the metal surface form mixed complexes of the type $[Al(OH)_xCl_y]^-$, which are more readily converted to the final product, $[Al(OH)_4]^-$, than the intermediate hydroxo complexes[19,20].

Combined Effects of Quaternary Ammonium Salts and Ca^{2+} Ions

We attempted to increase the inhibition effect of quaternary ammonium salts on Ȧ dissolution by adding $CaBr_2$, $CaCl_2$ or CaI_2 into the reaction solution, by analogy to the works of other authors[3,4,21]. The concentration of the halides was 10^{-5} or 10^{-4} mol dm^{-3}. The reaction was slowed down in all cases; the inhibition effect of Ca^{2+} ions was roughly additive with that of the quaternary ammonium salts (Table III).

The mentioned effect is probably due to simultaneous (cooperative) adsorption[21] of both sorts of cations to form a combined adsorption layer, which is probably more stable than the adsorption layer consisting solely of the ammonium ions, and which is responsible for the decrease of the reaction rate.

Influence of Quaternary Ammonium Salts on the Potential (OCP) of Al

To verify the assumed mechanism of inhibition, the potential of Al was recorded as a function of the time during the kinetic measurements. The results are shown graphically in Fig. 4. The potential course was qualitatively the same in every experiment: after a rapid initial increase a shallow minimum appeared on the potential curve, and after about 30 min of reaction the potential attained a stationary value (a similar behaviour was described in ref.[22]), which was shifted to more anodic

TABLE III
Combined influence of 10^{-3}M-$(C_4H_9)_4$BrN (TB) and Ca^{2+} ions on the dissolution of Al in NaOH and its stationary potential

Additive	$v^{(m)} \cdot 10^2$ kg m^{-2} h^{-1}	$v^{(V)}$ dm^3 m^{-2} h^{-1}	$I^{(m)}$ %	$I^{(V)}$ %	E_{st} V
10^{-3}M-TB + 10^{-5}M-Ca^{2+}	4·3	19·8	54·3	53·0	−1·309
10^{-3}M-TB + 10^{-4}M-Ca^{2+}	3·1	13·1	67·0	68·9	−1·302
10^{-5}M-Ca^{2+}	7·7	33·4	18·1	20·7	−1·311
10^{-4}M-Ca^{2+}	6·4	30·2	31·9	28·3	−1·307

values after addition of tetraalkylammonium salts. The stationary potentials, E_{st}, are given in Tables I and III.

The monotonical potential course can be discussed in terms of the formation of a steady state on the electrode surface, characterized by a uniform evolution of hydrogen, as described in our preceding work[23]. The shift of the stationary potential to more anodic values compared to the non-inhibited system is in accord with the discussed concept about retarding both the cathodic and anodic reactions by the addition of tetraalkylammonium salts.

REFERENCES

1. Cavallaro M.: Ind. Chim. Belg. *28*, 1256 (1963).
2. Horner L.: Chem.-Ztg. *100*, 247 (1976).
3. Kapali V., Venkitakrishna Iyer S., Subramanyan N.: Br. Corros. J. *4*, 305 (1969).
4. Krishnan M., Subramanyan N.: Corros. Sci. *17*, 893 (1977).
5. Desai M. N., Desai S. M., Gandhi M. H., Shah C. B.: Anti-Corrosion *18*, 9 (1971).
6. Miadoková M., Štětinová L.: Collect. Czech. Chem. Commun. *41*, 56 (1968).
7. Miadoková M., Petrtýlová J.: Chem. Papers *39*, 237 (1985).
8. Starks C. M.: J. Am. Chem. Soc. *93*, 195 (1971).
9. Paleček J., Šilhánek J.: Chem. Listy *77*, 113 (1983).
10. Hirai T., Yamaki J., Okada T., Yamaji A.: Electrochim. Acta *30*, 61 (1985).
11. Hirai T.: Denki Kagaku *54*, 356 (1986); Chem. Abstr. *105*, 64789 (1986).
12. Malát M.: *Absorpční anorganická fotometrie*, p. 286 and 291. Academia, Prague 1973.
13. Akimov G. V.: *Theorie a zkušební methody korose kovů*, p. 253. Státní nakl. tech. literatury, Prague 1953.
14. Miadoková M., Šiška J.: Collect. Czech. Chem. Commun. *52*, 1461 (1987).
15. Sundararajan J., Rama Char T. L.: Corrosion *17*, (1961).
16. Halaša I., Miadoková M.: Collect. Czech. Chem. Commun. *53*, 970 (1988).
17. Miadoková M., Molnárová-Plchová M.: Chem. Papers *39*, 229 (1985).
18. Macdonald D. D., Lee K. H., Moccari A., Harrington D.: Corros. Sci. *44*, 652 (1988).
19. Izotova S. G., Sysoeva V. V., Artyugina E. D.: Zh. Prikl. Khim. *9*, 2115 (1985).
20. Šiška J., Miadoková M., Vítková M.: Collect. Czech. Chem. Commun. *54*, 102 (1989).
21. Subramanyan N., Ramakrishnaiah K.: Indian J. Technol. *8*, 369 (1970).
22. Streicher M. A.: Trans. Electrochem. Soc. *96*, 184 (1949).
23. Halaša I., Miadoková M.: Collect. Czech. Chem. Commun. *55*, 345 (1990).

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