

Potential Sweep Voltammetry of Aluminium(III) Perchlorate in Dimethylformamide

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The nature of two voltammetric peaks of Al(III) in DMF was investigated. Following the changes in peak currents with varying concentration of depolarizer and scan rate the adsorption character of the electrochemical process in the positive peak was proved. For the negative peak the proportionality of the peak current to the concentration of depolarizer was found. The diffusion character of this process is applied only at scan rates higher than 2 V/s.

In water solution, the compounds of Al(III) are subjected to fast hydrolysis. This is a serious drawback for their investigation, polarographic or other. In more acidic solutions where the hydrolysis can be suppressed, the hydrogen wave interferes very closely with the Al(III) wave at the polarographic reduction. Despite these facts polarographic wave of Al(III) was used for analytical purposes [1–6]. A few attempts were made to use organic solvents as dimethylformamide and dimethyl sulfoxide (hereafter referred to as DMF and DMSO) [7–9] for electrochemical investigations of aluminium. However, no basic studies as to the nature of electrochemical behaviour of Al(III) in organic solvents were made.

In combination with fast sweep of potential at voltammetry organic solvents remove difficulties mentioned earlier and therefore are suitable medium for polarographic investigations of aluminium.

Experimental

The method used for investigations was cyclic voltammetry at the hanging mercury drop electrode (HMDE). Measurements were carried out on a Tektronix 564 oscilloscope with SSP-2 sweep polarographic analyzer. A three-electrode system was applied with an Ag|AgCl|KCl, KClO₄, DMF half cell as reference electrode [10] and with tungsten wire as counter electrode. A bridge made of methyl cellulose dissolved in saturated (TEAP) DMF [10] was used to connect the working solution with the reference electrode.

The best solubility of all aluminium salts in this medium showed aluminium(III) perchlorate. It was prepared by the action of 70% perchloric acid on 99.99% aluminium wire. The product was dried in a vacuum oven at 50–60°C for 48 hours after several evaporations with HClO₄.

DMF was purified as follows: Commercial DMF was shaken with solid potassium carbonate for 4 hours and filtered. It was then treated in the same way successively with potassium hydrogen sulfate, again with potassium carbonate and then with molecular sieves A5, and twice distilled under reduced pressure 10 mmHg at 55°C. The purified DMF was stored over molecular sieves.

Results

On the voltammogram of Al(III) perchlorate in DMF there appear two irreversible peaks on the cathodic scan. Their position on the potential axis changes with the rate of the voltage sweep. With successive cycles the height of both peaks diminishes. The positive peak (-2.2 V at scan rate 1 V/s) disappears after the first cycle completely. The negative one (-2.5 V at scan rate 1 V/s) disappears after a few cycles (5–25) the number of which depends upon the concentration of depolarizer and the scan rate applied.

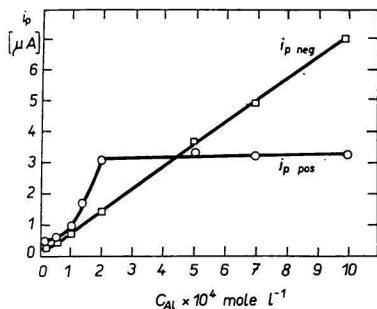


Fig. 1. The peak height of both voltammetric peaks of Al(III) perchlorate as a function of depolarizer concentration.

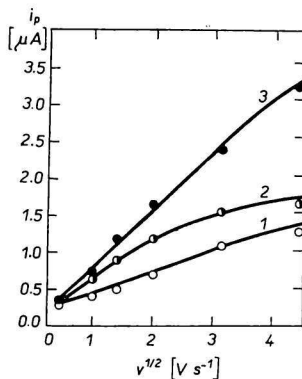


Fig. 2. Changes of positive peak current for different drop sizes with rate of voltage scan.

1–3. increasing drop size; concentration of depolarizer 5×10^{-5} M-Al(III).

The change of height of both peaks with increasing concentration of depolarizer in the first cycle is illustrated in Fig. 1. The positive peak height in the concentration range $1-2 \times 10^{-4}$ M of Al(III) is proportional to the depolarizer concentration. Above this value the peak current becomes independent of further increase of depolarizer concentration. The negative peak current is proportional to the depolarizer concentration in the whole measured range of concentrations except the concentration values less than 10^{-4} M-Al(III).

The peak height is also a function of the rate of voltage scan. This behaviour of Al(III) was studied at the concentration 5×10^{-5} M-Al(III) as well as at the concentration 10^{-3} M-Al(III). Three different drop sizes were used in order to study the influence of surface area changes.

In Figs. 2 and 3, respectively, the positive and negative peak currents are shown as a function of scan rate at various drop sizes. The positive peak current increases at these low concentrations continuously with increasing scan rate (Fig. 2) while the negative peak current (Fig. 3) is inhibited at high scan rates. This behaviour is most marked at big drops (curves 3 in both cases).

The change of the total current function $\sum i_p \cdot (cv)^{-1}$ with scan rate was followed ($\sum i_p = i_{p \text{ pos}} + i_{p \text{ neg}}$). This function presents a relative increase of total current at constant concentration of depolarizer. The comparison of the total current function for

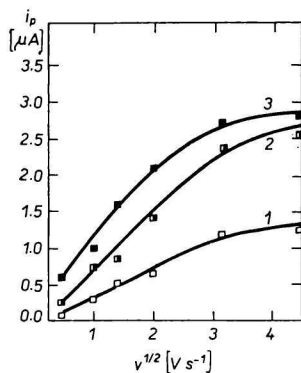


Fig. 3. Changes of negative peak current for different drop sizes with rate of voltage scan.

1—3. increasing drop size; concentration of depolarizer 5×10^{-5} M-Al(III).

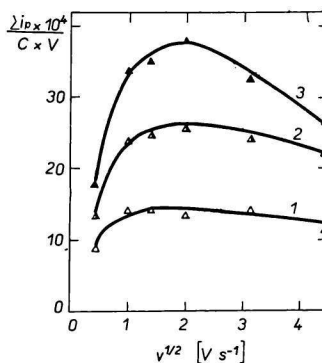


Fig. 4. Variation of total current function for different drop sizes with rate of voltage scan at low depolarizer concentrations 5×10^{-5} M-Al(III).

1—3. increasing drop size.

lower and higher concentration of depolarizer was made. The results are presented in Figs. 4 and 5. Again, at the small drops (curves 1) only a slight change of the function can be seen while at big drops remarkable changes of the total current function occur (curves 3). The total current function is rather monotonous at higher concentrations (Fig. 5) in contradistinction to its behaviour at low concentrations (Fig. 4).

In Fig. 6 the current function is shown at the concentration 10^{-3} M-Al(III) with increasing scan rate. The negative peak current function decreases to the value of scan rate 2 V/s and then remains constant. The positive peak current function does not change in the whole range of the measured scan rate values.

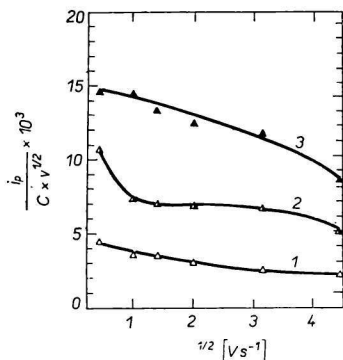


Fig. 5. Variation of total current function for different drop sizes with rate of voltage scan at higher depolarizer concentrations 10^{-3} M-Al(III).

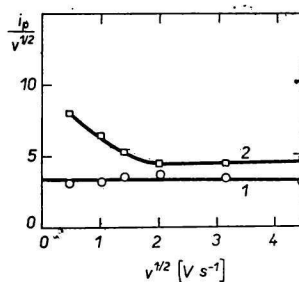


Fig. 6. The current function for positive peak (curve 1) and negative peak (curve 2) with rate of voltage scan. Depolarizer concentration 10^{-3} M-Al(III).

Discussion

The current decrease of both peaks with successive cycles is caused partly by the depletion of diffusion layer and partly by the fact that there occurs no reversible process on the anodic sweep so that no material is provided for the next cycle.

With increasing concentration of depolarizer the positive peak current increase is limited. This indicates the adsorption character of the process. When a concentration value is reached at which the whole electrode surface is covered by adsorbed material, a further increase in peak height is not possible. The adsorption character of the process is confirmed by the earlier observation that the positive peak disappears after the first cycle. The stationary electrode surface is occupied by the product of the previous adsorption in the first cycle and therefore no further adsorption is possible on the same drop. The separation of both peaks indicates strong adsorption. According to [11, 12] a strong adsorption of a product of electrochemical reaction takes place.

The negative peak current is proportional to depolarizer concentration, which would indicate a diffusion process in the given range of concentrations. According to *Randles—Ševčík* equation for diffusion current [13, 14], the current function $i \cdot v^{-1/2} = f(v)$ is a straight line parallel to the v axis. In Fig. 6 (curve 2) it is seen that this condition is fulfilled only for scan rates higher than 2 V/s. At lower scan rates the proper electrode reaction is complicated by a chemical reaction which causes an increase of the depolarizer concentration in the vicinity of electrode. This effect is also proportional to depolarizer concentration in the concentration range investigated. This is illustrated by the curve i_{neg} in Fig. 1. Thus, the lower is the depolarizer concentration and the higher is the scan rate, the more evident is the diffusion character of the negative peak current.

The influence of adsorption on the overall electrode process is given by several factors: the depolarizer concentration, the drop surface and the scan rate. With increasing scan rate the adsorption current increases faster than diffusion current (the adsorption current is proportional to v while the diffusion current is proportional to $v^{1/2}$) [12]. The adsorption peak increases to the detriment of diffusion peak. In limiting case at very high scan rates the diffusion peak disappears and the adsorption peak reaches the original diffusion peak height as well as diffusion character. This is the region, where the adsorption peak is governed by diffusion process because there is a shortage of depolarizer in the diffusion layer to cover the whole electrode surface, and the diffusion flow is the slowest process. This character of the adsorption process is the more evident, the lower is the depolarizer concentration (see the $i_{\text{p pos}}$ curve in Fig. 1 in the low concentration range) and the higher is the maximum surface coverage and the scan rate.

In Figs. 2 and 3 it is seen that at low concentrations of depolarizer (5×10^{-5} M) the adsorption current increases proportionally to v (Fig. 2) while the diffusion current stops increasing at high scan rates (Fig. 3). This effect is most marked at big electrode surfaces in agreement with the above said.

The observed character of electrode processes in both peaks is confirmed by the total current function plot in Figs. 4 and 5 as well. The total current increases at low concentrations with increasing scan rate (Fig. 4) due to the fast increase of the adsorption peak. As the scan rate further increases the diffusion flow proves insufficient especially at big drops (curve 3) and the current falls. At high enough concentrations the transport of depolarizer to the electrode is sufficient and the current decrease is much smaller. At the concentration 10^{-3} M-Al(ClO₄)₃ another phenomenon can be observed in connection with current function changes — a chemical reaction coupled to the charge transfer. By comparison of curve 2 in Fig. 6 (negative peak current function) and curve 2 in Fig. 5

(total current function under the same conditions as to the drop size and depolarizer concentration) it becomes obvious that it is the negative peak decrease that contributes mainly to the decrease of total current at lower scan rates.

Thus, the polarographic reduction of aluminium salts in DMF is a complicated process and is influenced by many factors. However, the interference of hydrogen wave is eliminated. The extent of solvolysis is negligible [15] especially if only the first cycle of voltammetric record is taken into account.

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