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Extraction of gallium metal by exchange reaction between sodium amalgam and Ga(III): a cyclic voltammetric study

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A novel method of investigating the basic aspects of a gallium recovery process by a cyclic voltammetric method is described. This allowed the study of the exchange reaction between Ga(III) and sodium amalgam as a function of amalgam and gallium concentration, among others, in a simple and direct manner, thereby offering a convenient method for optimizing gallium recovery process variables.

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1. Introduction

The interest in the recovery of gallium metal arises from its unique properties and its expanding uses in solid-state electronic devices, the nuclear industry and optics. Gallium, invariably associated with bauxite, is taken into sodium aluminate solution as sodium gallate during the digestion of bauxite with alkali. Its concentration in the liquor is very low and so the extraction of gallium is mainly carried out by an amalgam metallurgical process using a mercury or sodium amalgam cathode and a steel anode in an electrolytic cell. A review of the growth of electrohydrometallurgical processes for extracting gallium from sodium aluminate lyes up to 1978 may be found [1].

Earlier workers have found that when the sodium aluminate liquor is electrolysed using a mercury cathode, sodium ions are first discharged at the cathode yielding sodium amalgam and, later, the gallium present in solution passes into the mercury phase through an exchange reaction taking place between sodium in the amalgam and gallium in the solution. Although the recovery of gallium by this method has been practised over the years, there have been few studies on the basic aspects pertaining to the underlying displacement reaction [2–5]. Such basic information is vital to the optimization of experimental conditions. A recent report by Kozen *et al.* [6] suggests, from results using an anodic stripping technique, that a secondary phase exchange reaction is operative in gallium recovery.

This communication presents the results of a systematic study of the reaction between sodium in amalgam and gallium in solution using a cyclic voltammetric technique on a hanging mercury drop electrode in a solution of alkaline gallate. The study of the displacement (or exchange) is made by a novel method, namely a cyclic voltammetric scan involving *in situ* deposition of sodium by extending the sweep potential to the deposition potential of sodium during the cathodic sweep of the cyclic voltammogram branch.

2. Experimental details

A conventional all-glass electrolysis cell having a three-electrode assembly with provision for inlet and outlet for deaerating the solution with pure N_2 gas was used. A three-electrode system consisting of a hanging mercury drop electrode supplied by Metrohm of Switzerland, a mercury pool counter electrode and a reference electrode of Hg–HgO in 1 M NaOH were employed. All the solutions were prepared from Analar grade reagents and twice-distilled water. Sodium gallate solutions corresponding to gallium concentrations 0.7×10^{-3} M to 5.7×10^{-3} M in 0.1–2.0 M NaOH were employed. The sodium

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gallate solutions of the required strength were prepared by electrolysing a gallium pool (99.9% pure) anode and a platinum cathode using a current density of 30–50 mA cm^{-2} in an all-glass cell in which the cathode and anode compartments were separated. The desired solution, having been deaerated using pure nitrogen (free from oxygen), was introduced into the cell. The cyclic voltammograms were then run on the systems chosen for study. The range of potential covered was -0.8 to -2.2 V (Hg–HgO) (to cover the deposition and dissolution of both gallium and sodium). The starting potential for all the cyclic voltammetric experiments was -0.8 V from where the cathode potential sweep was effected. The potential was reversed to obtain the anodic branch of the cyclic voltammogram, such reversal being effected at different chosen values of the potentials in the individual experiments.

A Wenking (Model LB 75M) potentiostat coupled with a Wenking Scan generator (Model VSG 72) was used for controlling the potential. An *X–Y* recorder (Digitronic Model 2000 series) was used to record the *i–E* curves. All the potentials were expressed versus Hg–HgO in 1 M NaOH and the measurements made in deaerated solutions at 32 ± 1° C.

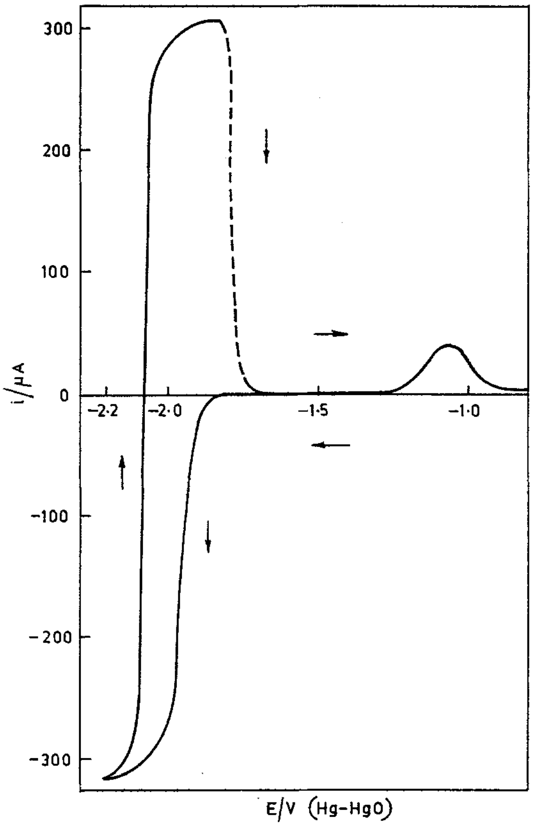

Fig. 1. Cyclic voltammetric curve on hanging mercury drop electrode for a solution containing 4.3×10^{-3} M gallium in 0.1 M NaOH. Sweep rate, 20 mV s^{-1}; range of the potential sweep, -0.8 to -2.2 V (versus Hg–HgO).

3. Results and discussion

Cyclic voltammetric experiments for the system alkaline gallate on a hanging mercury drop electrode have been carried out using gallium concentrations corresponding to 0.7×10^{-3} to 5.7×10^{-3} M in different alkali strengths, namely 0.1–2 M NaOH. These experiments yielded reproducible and well-defined current potential curves.

The typical cyclic voltammetric response of a sodium gallate solution containing 4.3×10^{-3} M gallium in 0.1 M NaOH is shown in Fig. 1. The cyclic voltammetric curve for the solution without gallium is also recorded under identical experimental conditions and is shown in Fig. 2 for comparison.

The deposition and dissolution of sodium in the potential range -1.7 to -2.2 V can be clearly seen from the large cathodic and anodic peaks in Figs 1 and 2. It can also be observed from Fig. 1 that a well-defined anodic peak for gallium dissolution is realized at the concentration of gallate employed. It is also seen from Fig. 1 that no measurable cathodic peak is obtained under these conditions. It is instructive to note that anodic dissolution currents for gallium obtained in the absence of sodium deposition have been found to be insignificant when compared to those obtained with sodium deposition included. Therefore under the cyclic voltammetric conditions reported it may be seen that dissolution of gallium arises essentially due to the availability of gallium enriched through the sodium exchange reaction as discussed below.

When a cyclic voltammogram is run with the inclusion of sodium deposition potential on a hanging mercury drop electrode–working electrode in sodium gallate solution it is expected that, in addition to the direct discharge of

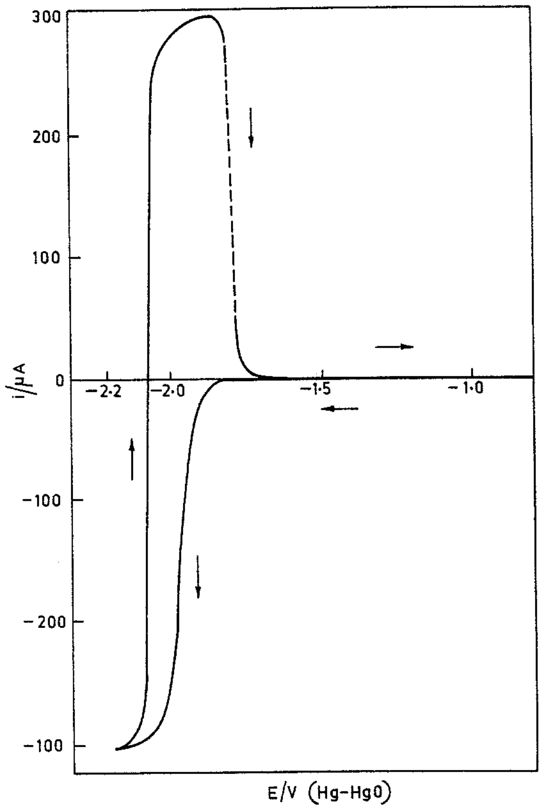

Fig. 2. Cyclic voltammetric curve on hanging mercury drop electrode for a solution containing 0.1 M NaOH. Sweep rate, 20 mV s^{-1}; range of the potential sweep, −0.8 to −2.2 V (versus Hg–HgO).

gallium, on mercury, gallium in solution also passes into the mercury phase. This takes place via a displacement reaction occurring between the sodium in the amalgam (formed *in situ*) and gallium in solution according to the equation [6]:

$$Na_3(Hg)_x + GaO_2^- + 2H_2O \rightleftharpoons Ga(Hg)_x + 3NaOH + OH^- \qquad (1)$$

If the possibility of an exchange reaction according to the above equation were taken into consideration, one might expect that the amount of gallium accumulated in the mercury phase should depend on:

(i) the amalgam concentration used (i.e. the amount of sodium in the amalgam)

(ii) the time of contact of the sodium amalgam with the solution containing gallium

(iii) the turbulence created on the amalgam surface among others.

The various experimental findings discussed below give support to the above.

The typical influence of gallate concentration and alkali concentration in solution is demonstrated in Figs 3 and 4, respectively. The typical cyclic voltammetric response of the effect of gallium concentration on the anodic peak height obtained for a fixed alkali concentration (namely 0.5 M NaOH) with varying gallium concentration

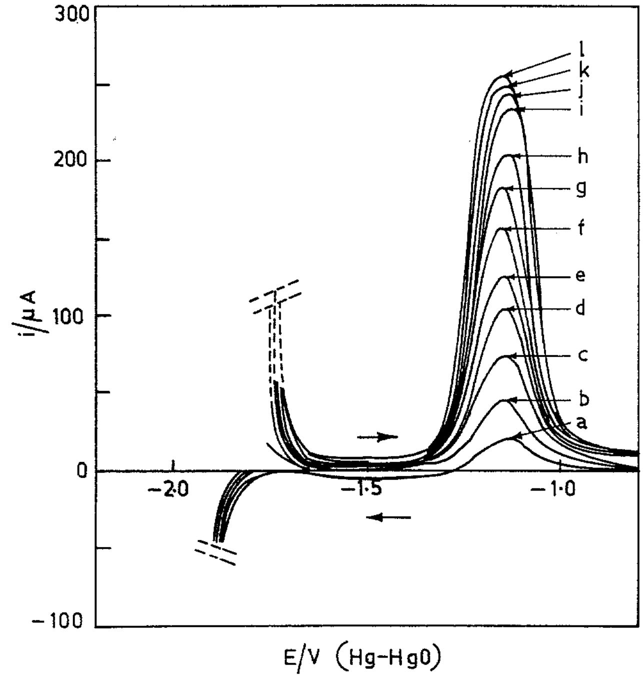

Fig. 3. Effect of gallium concentration on the anodic peak height of cyclic voltammetric curves on hanging mercury drop electrode for a solution containing (a) 1.4, (b) 2.8, (c) 4.3, (d) 5.7, (e) 7.1, (f) 8.8, (g) 10, (h) 11.4, (i) 12.9, (j) 14.3, (k) 15.7 and (l) 18.6 × 10^{-3} M gallium in 0.5 M NaOH. Sweep rate, 20 mV s^{-1}; range of the potential sweep, −0.8 to −2.2 V (versus Hg–HgO).

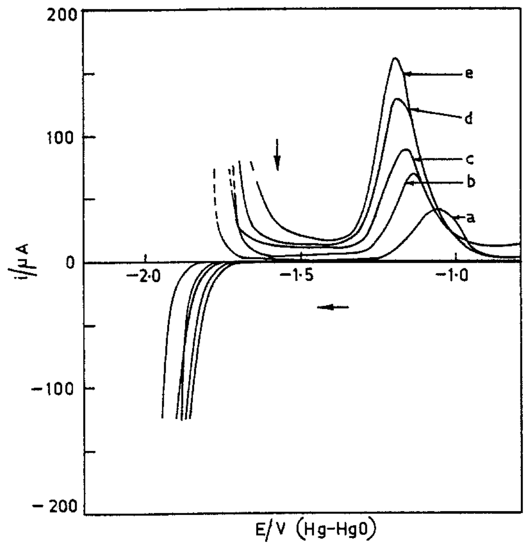

Fig. 4. Effect of alkali concentration on the anodic peak height of cyclic voltammetric curves on hanging mercury drop electrode for a solution containing 4.3 × 10^{-3} M gallium. Sweep rate, 20 mV s^{-1}; range of the potential sweep, −0.8 to −2.2 V (versus Hg–HgO). NaOH concentration: (a) 0.1 M, (b) 0.5 M, (c) 1.0 M, (d) 1.5 M, and (e) 2.0 M.

in solution is given in Fig. 3. It is clear that the magnitude of the anodic peak obtained is proportional to the gallate concentration for a fixed alkali strength and is proportional to the sodium strength (present as sodium hydroxide) for a fixed gallate concentration. Fig. 4 depicts the latter effect for a given concentration of gallium in alkaline solution more vividly. Fig 3 shows that the anodic peak potential is nearly independent of the gallium concentration, while in the case of alkali concentration the potentials recorded are slightly dependent on the alkali strength (see Fig. 4) and are found to shift in a more cathodic direction with increase in alkali strength. It can also be seen from Fig. 4 that for a given gallium concentration the anodic peak height rises with alkali strength at a fixed sweep rate under the experimental conditions employed. The linearity between the peak height and the alkali strength at various sweep rates employed is given in Fig. 5. All the above observations point to the involvement of the exchange reaction between the sodium deposited *in situ* and the gallate in solution. Thus increased gallate concentration in solution for a fixed alkali or increased alkali strength (which means the availability of a large sodium ion concentration in solution, which in turn reflects sodium amalgam formation) for a fixed gallate strength would favour the formation of higher concentrations of gallium amalgam. The experimental observations are consistent with the above expectations.

The relationship between the time of contact of the amalgam and the solution containing gallate can be inferred from the experimental results involving the influence of the sweep rate as follows. Fig. 6 represents the effect of sweep rate on the anodic peak height for a solution containing a given concentration of gallium in 2 M NaOH. It is clear from Fig. 7 that the peak heights are inversely proportional to the sweep rates employed. This may be understood in terms of the favourable conditions for build-up of large sodium amalgam concentrations and

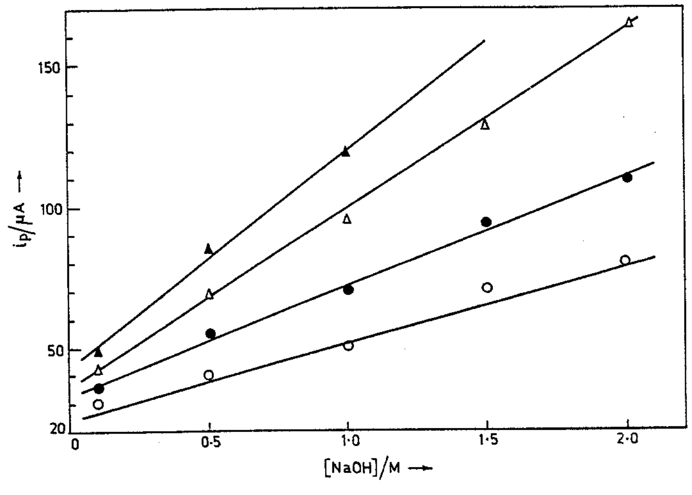

Fig. 5. Plot of i_p versus NaOH concentration for a solution containing 4.3 × 10^{-3} M gallium at different sweep rates, i.e. ○, 60; ●, 40; △, 20; ▲, 10 mV s^{-1}. Range of the potential sweep, −0.8 to −2.2 V (versus Hg–HgO).

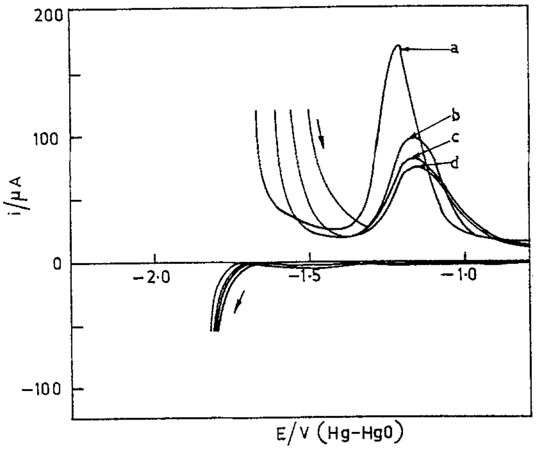

Fig. 6. Effect of sweep rate on the anodic peak height of cyclic voltammetric curves on hanging mercury drop electrode for a solution containing 3.5×10^{-3} M gallium in 2 M NaOH. Range of the potential sweep, −0.8 to −2.2 V (versus Hg–HgO). Sweep rates (a) 20, (b) 40, (c) 60 and (d) 80 mV s^{-1}.

large times of contact that could result at lower sweep rates, yielding larger exchange between sodium and gallate to give maximum currents under low sweep rate conditions. Such inverse dependence of i_p on v (sweep rate) in a number of solutions of different alkali strength using the same gallium concentration is given in Fig. 7. Further, the increased current under low sweep rate conditions, whose magnitude varies in direct proportion to alkali strength, may be expected to reach some limiting values for a given concentration of alkali. Such expectation is, of course, based on the accumulation of sodium metal *in situ* in the mercury to a saturation level that may dictate the highest limit for the gallium exchange reaction for given experimental conditions (namely volume of mercury drop and sweep rate). Data given in Fig. 8 corresponding to the anodic peak height for various gallium concentrations in 0.5 M alkali confirm such expectations.

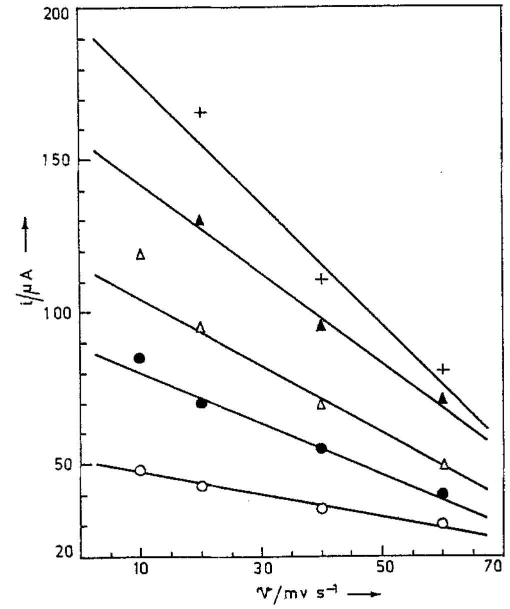

Fig. 7. Plot of i_p versus v for a solution containing 4.3×10^{-3} M gallium for different concentrations of NaOH, i.e. ○, 0.1; ●, 0.5; △, 1.0; ▲, 1.5; +, 2.0 M NaOH. Range of the potential sweep, −0.8 to −2.2 V (versus Hg–HgO).

It is noted from the above cyclic voltammetric data in dilute gallate solutions that gallium could be accumulated through the exchange reaction to appreciable levels, and under similar experimental conditions the accumulation of gallium by direct discharge of gallate is found to be negligible.

It may also be pointed out that the observed enhancement in the anodic signal for gallium does not arise merely because of the agitation resulting from the high sodium deposition current or convective movements on mercury drop, as independent experiments involving interaction of the sodium amalgam with gallate in the absence of external current have given conclusive evidence about the phase exchange [6, 7].

Finally, we illustrate the use of the present approach involving *in situ* deposition of sodium to investigate the effect of organic impurities

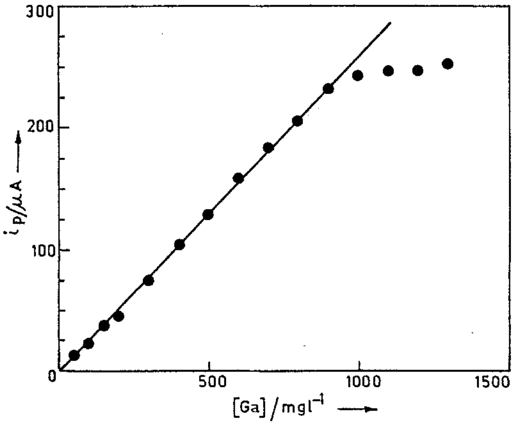

Fig. 8. Plot of anodic peak height versus gallium concentration in 0.5 M NaOH. Sweep rate 20 mV s^{-1}; range of the potential sweep, −0.8 to −2.2 V (versus Hg–HgO).

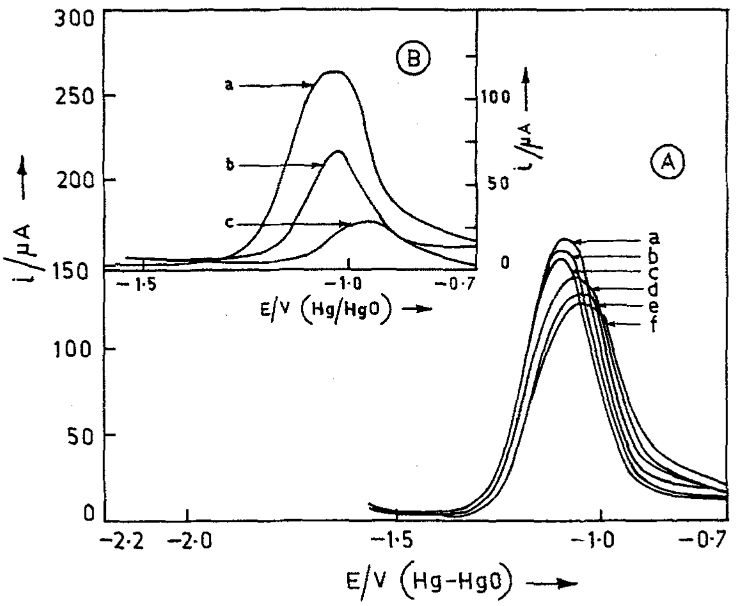

Fig. 9. (A) Cyclic voltammetric curves obtained for solutions containing varying oxalic acid concentrations in a solution containing $250\,mg\,l^{-1}$ gallium in 0.5 M NaOH. Sweep rate $20\,mV\,s^{-1}$. Oxalic acid concentrations: (a) 0, (b) 0.1, (c) 0.5, (d) 1.0, (e) 1.5 and (f) $2.0\,g\,dm^{-3}$. Range of the potential sweep, −0.8 to −2.2 V (versus Hg–HgO). (B) Same as A but containing different benzoic acid concentrations: (a) 0.1, (b) 0.5, (c) $1.0\,g\,dm^{-3}$.

which are known to adversely affect the gallium recovery. The typical influence of aliphatic and aromatic organic compounds, namely oxalic acid and benzoic acid, is demonstrated in Fig. 9. It is clear from the magnitude of the anodic peaks obtained in the presence of oxalic acid (see Fig. 9A) and benzoic acid (see Fig. 9B) that inferences can be drawn on the relative influences of these acids on the recovery of gallium. These observations are in accordance with the earlier report made by Solymer *et al.* [2] on the effect of these organic compounds present in the solution on the gallium accumulation during electrolysis. More detailed studies on the above aspects are in progress.

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