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Effect of impurities on gallate reduction in alkaline solution — a linear stripping voltammetry study

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Industrial production of gallium is mainly carried out by the electrolytic method using Bayer liquors of the aluminium industry. The major impediment to the effective recovery of gallium is known to be the presence of impurities (metallic and organic). Investigations on the effect of organics (aliphatic and aromatic) employing linear stripping voltammetry techniques on glassy carbon electrodes in alkaline gallate solutions revealed the inhibitive effect of these compounds on the electrodeposition of gallium and, hence, on gallium recovery from aluminate liquors.

1. Introduction

Gallium is recognized as an important metal in the electronics and semiconductor industries. It is extracted universally from alkaline solutions of Bayer liquor of the aluminium industry. Its recovery from coal fly-ash and zinc ores are also known [1], but these sources are of little industrial importance. Popova has reviewed the growth of electrohydrometallurgical processes for extracting gallium from alkaline aluminate solution up to 1978 [2].

By virtue of the close similarity of its atomic radius with the atomic radius of aluminium, gallium is invariably associated with the aluminium ore. When the ore is digested with alkali, gallium is taken into sodium aluminate solution as sodium gallate wherein it attains an equilibrium concentration of about 250 mg dm^{-3}. Depending on the nature and origin of the bauxite ore, sizeable quantities of inorganic and organic materials go into the solution during the digestion with alkali. Their concentration builds up in the circulating plant liquors at the time of digestion because of successive recyclings.

Gallium is extracted from aluminate liquors using techniques such as solvent extraction [3–5] and cementation with sodium amalgam [6, 7], the latter being the commercially adopted method at present. It is well known that cementation is carried out by electrolysing sodium aluminate liquor containing gallium using pure mercury (or sodium amalgam) as cathode and a mild steel plate as anode. When the liquor is electrolysed sodium ions are first discharged at the cathode yielding sodium amalgam and, later, the gallium present in solution passes into the mercury through displacement yielding Na–Ga–Hg amalgam. The resultant amalgam is subjected to denudation to obtain sodium gallate solution. The gallate solution is then concentrated, which on electrolysis using a suitable solid cathode yields gallium metal.

Thus, gallium recovery from Bayer liquor comprises gallium deposition as an amalgam, denudation of the amalgam to obtain sodium gallate solution and electrolysis to give gallium metal. The amalgamation as well as the final gallate electrolysis are critically affected by the presence of inorganic and organic impurities in solution [8–13].

The effect of heavy metals such as Fe, Mo, V and W, as well as common organic acids, viz. formic, acetic, succinic and oxalic acids normally found as impurities in Bayer liquor, in inhibiting gallium deposition into Hg, Na/Hg and solid cathodes, has been investigated using voltammetric techniques [14, 15].

The main object of this work is to present the results of a systematic study of the effect of organic impurities on gallate reduction in alkaline medium using a linear stripping voltammetric technique and rotating glassy carbon disc working electrodes and to interpret these results with particular reference to the recovery of gallium.

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, dried nitrogen gas was used. The three-electrode system consisted of (i) a rotating Teflon shrouded glassy carbon disc (6 mm diameter) working electrode, (ii) a platinum counter electrode and (iii) a Hg/HgO in 1 M NaOH reference electrode.

All the solutions were prepared from AnalaR grade reagents and double distilled water. Sodium gallate solution corresponding to a gallium concentration of 4.3×10^{-3} M in 0.5 M NaOH was employed. The sodium gallate solutions of the required strength were prepared by dissolving gallium oxide (JMC Grade 2) in alkaline solution. The desired solution, having been deaerated using pure oxygen-free nitrogen, was introduced into the cell. The gallium metal was deposited onto the rotating glassy carbon electrode with and without the presence of organics in solution at -2.0 V for 1 min and the electrode was then subjected to an

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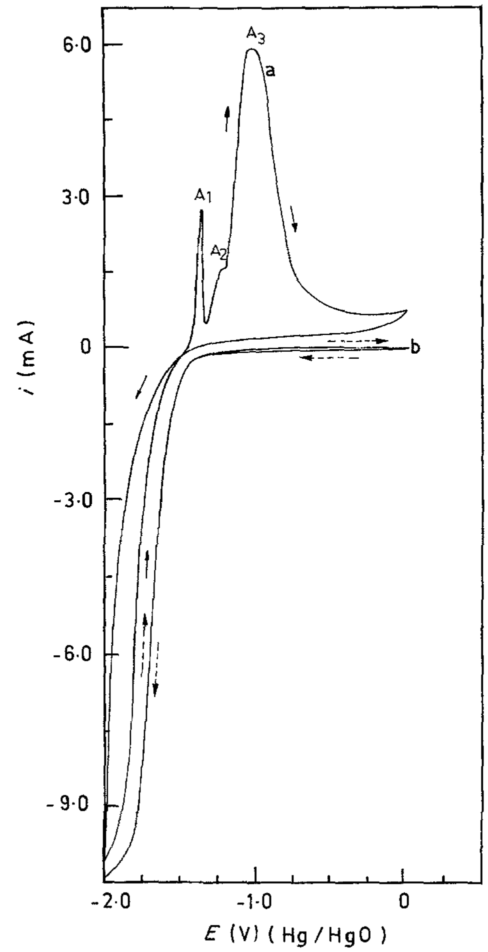

Fig. 1. (a) Cyclic voltammetric stripping curve on glassy carbon electrode after electrolysis at -2.0 V for 1 min in 4.3×10^{-3} M gallium in 0.5 M NaOH. Scan rate 50 mV s^{-1}. $\omega = 750$ rpm. Range of potential sweep -2.0 to 0.0 V (vs Hg/HgO). (b) As (a) but without gallium in solution.

anodic sweep. The gallium deposition efficiency was calculated by computing the charge under the anodic peak. Before depositing gallium, the exposed circular cross section of the glassy carbon rod was polished with fine emery paper (4/0 grade), degreased with acetone and finally washed with twice distilled water.

Although it is known that the gallium recovery efficiency from alkaline solution is adversely affected by organic impurities present in it, little is known about the actual organic compounds that inhibit the above process. Hence, the organic matter present in actual Bayer liquor is extracted in acidic medium using ethyl ether, and subjected to evaporation on a boiling water bath. The resultant product, after treatment with chloroform, is analysed in order to identify the organic functional groups present using IR spectra. It is noted that the organics are aromatic in nature and possess phenolic and amino functional groups. Therefore, a number of organics were chosen, among which representative compounds containing the above functional groups are also included in the present study. These were oxalic acid, ascorbic acid, urea, benzoic acid, nitrobenzoic acid, *p*-amino toluene and metanilic acid. These compounds were added to the gallate solutions individually to ascertain their influence on gallium deposition.

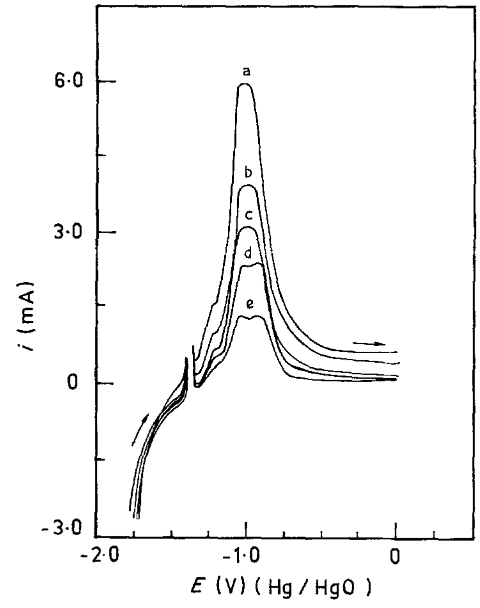

Fig. 2. Effect of oxalic acid concentration on the stripping curve obtained after electrolysis at -2.0 V for 1 min in 4.3×10^{-3} M gallium in 0.5 M NaOH. Scan rate 50 mV s^{-1}. $\omega = 750$ rpm. Range of potential sweep -2.0 to 0.0 V (vs Hg/HgO). Oxalic acid concentrations: (a) 0; (b) 3; (c) 9; (d) 15; (e) 21 g dm^{-3}.

A Wenking (Model LB 75 M) potentiostat coupled with a Wenking Scan generator (Model VSG 72) was used for controlling the potential. A Tacussel rotating electrode set-up (type EAD – 10,000) was used for controlling the rotation of the working electrode. An *x–y* recorder (Digitronic Model 2000 series) was used to record the *i–E* curves. All the potentials were expressed vs Hg/HgO in 1 M NaOH and the measurements were made in deaerated solutions at 25 ± 1°C.

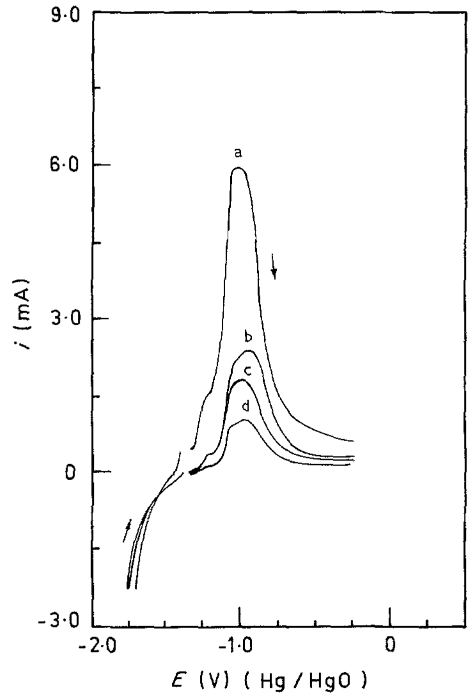

Fig. 3. Effect of ascorbic acid concentration on the stripping curve obtained after electrolysis at -2.0 V for 1 min in 4.3×10^{-3} M gallium in 0.5 M NaOH. Scan rate 50 mV s^{-1}. $\omega = 750$ rpm. Range of potential sweep -2.0 to 0.0 V (vs Hg/HgO). Ascorbic acid concentrations: (a) 0; (b) 3; (c) 6; (d) 9 g dm^{-3}.

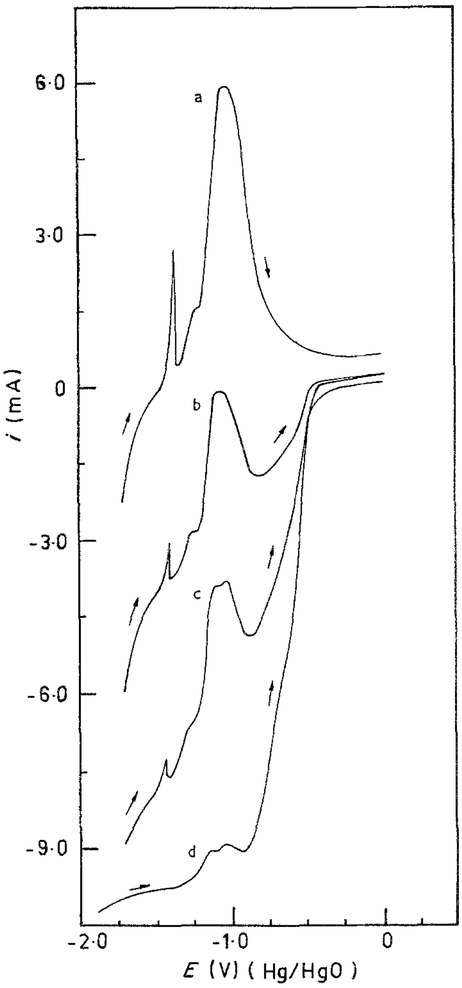

Fig. 4. Effect of nitrobenzoic acid concentration on the stripping curve obtained after electrolysis at −2.0 V for 1 min in 4.3 × 10^{-3} M gallium in 0.5 M NaOH. Scan rate 50 mV s^{-1}. ω = 750 rpm. Range of potential sweep −2.0 to 0.0 V (vs Hg/HgO). Nitrobenzoic acid concentrations: (a) 0; (b) 1; (c) 2; (d) 3 g dm^{-3}.

3. Results and discussion

The typical cyclic voltammetric response after constant potential deposition at −2.0 V vs Hg/HgO for 1 min from a sodium gallate solution containing 4.3 × 10^{-3} M gallium in 0.5 M NaOH is given in Fig. 1 (curve a). For comparison the response of the same solution containing zero gallium concentration was recorded under identical experimental conditions and is also shown in Fig. 1 (curve b).

It is seen from Fig. 1 that three anodic oxidation peaks (shown as A1, A2 and A3) are realized at about −1.4, −1.2 and −1.1 V, respectively. These three peaks arise due to the anodic stripping of the preconcentrated gallium in three stages [16, 17]. During the cathodic scan gallium deposition is seen to take place along with hydrogen evolution at extreme negative potentials ($\geqslant$1.8 V). It is seen from the results obtained with the addition of different organics that the stripping peak A3, which is the predominant one among the three peaks, clearly reveals the inhibiting influence of the organic.

Figures 2, 3 and 4 illustrate such typical influence in the cases of oxalic acid, ascorbic acid and nitrobenzoic acid, respectively. Similar observations have been recorded using aromatic and aliphatic organics; benzoic acid, *p*-amino-toluene, metanilic acid and urea yielded similar results. The observation of the magnitude of the anodic peaks obtained and the charge computed in these cases (which are found to be in proportion to the gallium deposition), are seen to be dependent on the concentration of the impurities present in the solution. Figure 5 illustrates this observation clearly.

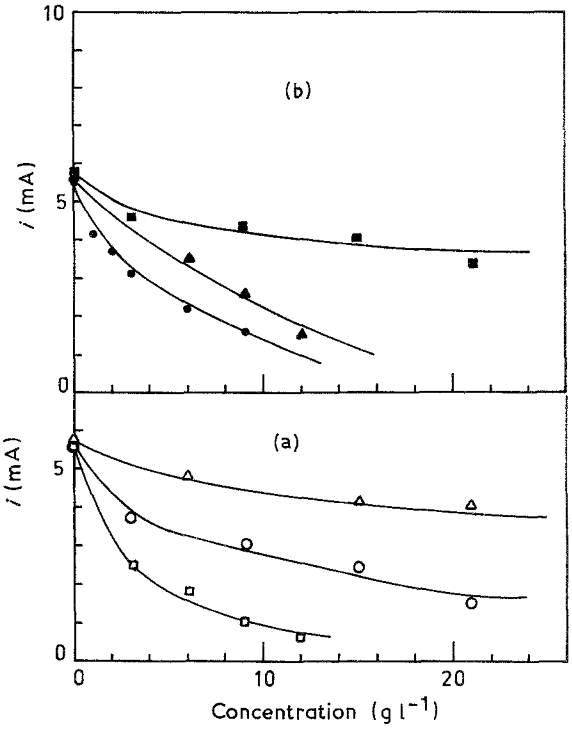

Fig. 5. (a) Plot of i_p vs concentrations of aliphatic organics in a solution containing 4.3 × 10^{-3} M gallium in 0.5 M NaOH. ○, Oxalic acid; □, ascorbic acid; △, urea. (b) Plot of i_p vs concentrations of aromatic organics in a solution containing 4.3 × 10^{-3} M gallium in 0.5 M NaOH. ■, Benzoic acid; ▲, *p*-amino toluene; ●, metanilic acid.

It is seen, in the case of the compounds urea and benzoic acid, that there is a reduction in the charge observed (under A3) initially, followed by its relative insensitivity to concentration of the organics added (Table 1 and Fig. 5). But with other organic impurities studied it is observed that increasing the concentration of the impurities reduces the deposition efficiency for gallium accumulation, the extent of reduction and the influence of concentration being characteristic of the organic compound investigated.

Among the organics studied, inhibition due to nitrobenzoic acid is found to be the most remarkable on gallium recovery (see Fig. 5). With as low a concentration as 1 g dm^{-3} of this organic the gallium recovery is affected substantially (Table 1 and Fig. 5). It is also seen from the anodic stripping curve that the gallium stripping peak appears below the zero current line in the presence of 1 g dm^{-3} concentration of nitrobenzoic acid, and the recovery of gallium is practically nil if the concentration exceeds 5 g dm^{-3}.

To establish whether organic addition brings about a reduction in the hydrogen evolution potential and makes the cathodic reactions (gallium deposition

Table 1. Charge (Q, mC cm^{-2}) calculated under the stripping peak, A3, with and without the organics in solution. Deposition time: 2 min; deposition potential: −2.0 V; scan rate: 50 mV s^{-1}; ω = 750 rpm; range of potential sweep: −2.0 to 0.0 V (vs Hg/HgO)

Concentrations of organic (g dm^{-3})	Q *(mC cm^{-2})*						
	Oxalic acid	*Ascorbic acid*	*Urea*	*Benzoic acid*	*Nitrobenzoic acid*	*Metanilic acid*	*p-Aminotoluene*
0	22.5	22.5	22.5	22.5	22.5	22.5	22.5
5	16.5	12.2	20.9	20.6	2.6	16.5	14.6
10	–	6.1	20.5	–	–	13.2	10.6
15	12.2	3.4	–	18.9	–	6.1	7.9
20	–	1.6	–	–	–	–	–
25	10.9	–	20.5	18.5	–	–	–
35	–	–	18.5	15.1	–	–	–

and hydrogen evolution) more in favour of hydrogen evolution (thus accounting for lower efficiency of gallium deposition), data were collected on the hydrogen evolution potential in alkaline solution containing various organics studied and these are presented in Table 2. While it is easy to see the pronounced effect of the hydrogen evolution reaction in the case of nitrobenzoic acid and the considerable effect, even in the case of *p*-nitrotoluene and metanilic acids, the same is not apparent in the case of ascorbic acid, oxalic acid, benzoic acid and urea. Factors other than the reduction in the HER potential in the presence of organics (such as adsorbed organic layers) may be operative, and need further study.

Splitting of the anodic peak A3 is generally noticed at high concentration of the organic and this may be associated with the reduction of two different species of trivalent gallium.

Table 2. Effect of organics on the hydrogen evolution potential on GCE in alkaline media

	Hydrogen evolution potential (V vs Hg/HgO)
Pure alkali	−1.500
Oxalic acid	−1.475
Urea	−1.425
Ascorbic acid	−1.500
Benzoic acid	−1.500
Nitrobenzoic acid	−0.450
p-Nitrotoluene	−1.425
Metanilic acid	−1.250

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