AMALGAM CATHODE IN VOLTAMMETRY

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POLAROGRAPHY using amalgam anodes has been studied, particularly in relation to stripping analysis. The use of amalgam cathode is rather limited, because of the difficulty of obtaining meaningful results on the conventional d.c. polarographs. This study is now possible using the fast voltage scanning instruments such as cathode ray polarographs.

The study of amalgam cathode will throw some light on the mechanism of electrode reaction. The fundamental electrode reduction process on DME can be written as

$$M^{+n} + ne \rightleftharpoons M \qquad (1)$$

and if the metal dissolves in mercury, it can further be written as

$$M + Hg \rightleftharpoons M\ (Hg) \qquad (2)$$

These two equations can be combined together to form a composite equation

$$M^{+n} + ne + Hg \rightleftharpoons M\ (Hg) \qquad (3)$$

If then instead of mercury, an amalgam is taken as cathode, then the forward reaction may be slowed down. This will be particularly true of the reduction of the cation, which forms the amalgam in cathode, namely the reduction of cadmium ions on the cadmium amalgam cathode. It will also be interesting to study the other amalgam forming cation reduction on cadmium amalgam as well as the reduction of non-amalgam forming ions such as chromate, etc.

A 50 ml. pyrex beaker fitted with a rubber bung with perforations for inserting electrodes and bubbling and exit of nitrogen serves as the polarographic cell.[1] The electrodes system used as J type mercury pool cathode (0·1215 cm.^{2}, area) and molybdenum wire reference electrode (1·5 cm. long, 22 s.w.g.). The reduction was followed on the Differential Cathode Ray Polarograph, model A 1660, manufactured by the Southern Analytical Ltd., England. The temperature was kept constant at 30 ± 0·1° C. by an electronically operated thermostat. The supporting electrolyte used is 0·1 M potassium chloride prepared from AnalaR grade reagent All the other solutions were prepared from their AnalaR grade reagents and standardised in the usual way. Various concentrations of cadmium amalgam were prepared by weighing AnalaR grade cadmium metal and adding it to the weighed quantity of double distilled mercury. It was then placed on the water-bath covering it with 0·1 N sulphuric acid and the solution was allowed to take place for forty-five mintes to one hour.[10] The cadmium amalgam thus formed was kept under 0·1 N sulphuric acid solution. Before filling the amalgam in the J electrode, it was first washed with distilled water and then dried on the filter-paper. Compared to the dropping amalgam electrode, the quantity of amalgm required for the J type electrode is considerably smaller. Molybdenum reference electrode, which is being extensively used in our laboratory,[2-9] is found to be very useful in this work.

The results obtained for different cation reductions using different cadmium amalgam concentrations for cathode are given in Table I.

TABLE I

Wave characteristics obtained for cadmium amalgam cathode

Cathode : J type pool (area—0·1215 cm.^{2}). Anode : Mo wire (1·5 cm., 22 s.w.g.)
Ion concentration : 1×10^{-4}M. Supporting electrolyte 0·1M KCl.

i_p μ amp for % amalgam				Ion	E_p, V for % amalgam			
0·0	0·1	0·5	2		0·0	0·1	0·5	2·0
19·0	16·0	13·2	12·6	Cd^{++}	−0·58	−0·86	−0·85	−0·89
66·8	20·4	20·0	8·0	Cu^{++}	−0·20	−0·26	−0·60	−0·00
38·2	27·0	14·5	5·1	Ni^{++}	−1·1	−1·20	−1·22	−1·18
68·8	38·2	3·0	0·70	Zn^{++}	−1·06	−1·07	−1·17	−1·16
				Fe^{+++}	−1·57	−1·67	−1·75	−1·88
Current is unstable								
109·7	erratic	−64·0	30·0	Sb^{+++}	−0·47	−0·47	−0·61	−0·45
		24·0	erratic				−0·86	−0·71
28·0	36·4	9·0	..	CrO_4^{--}	−0·34	−0·26	−0·87	..
53·4	76·4	10·0	..		−1·20	−1·40	−1·17	..
400·9		45·0	76·0		−1·80	..	−2·00	−2·0

It is clear that for all the ions, the peak potentials shift towards negative side with the increasing cadmium amalgam concentration, the shift being very small for zinc and nickel. For cadmium reduction, even for 0·1% amalgam, the peak potential shifts by −0·30 V., but then remains nearly constant upto 2% amalgam. A shift of −0·40 V. occurs for copper only at 0·5% amalgam but remains constant thereafter. For iron, a maximum shift of 32 mV is obtained upto 2% amalgam. No change occurs for antimony upto 0·1%, but the reduction process splits into two steps thereafter. For chromate where three peaks are obtained for mercury electrode, the pattern is irregular, two peaks being obtained for 0·1%, three for 0·5% and one only for 2% amlagam concentration.

Kozlovskii and Bukhman reported that when metals in solution were more electropositive than metals in amalgam, a considerable change of half wave potential towards negative was observed.[11] In the present study, cadmium which is used as amalgam in cathode, occurs above copper and nickel in the electrochemical series, but is below zinc and iron.[12] Yet irrespective of their positions, the shift in each case is invariably towards the negative side.

The peak currents generally decrease with increasing amalgam concentration. The minimum decrease of 6·4 μ amp occurs in the case of cadmium reduction, and the maximum decrease of 68 μ amp occurs in the case of zinc. Whereas the peak potentials are not much affected for 0·1% amalgam, the peak currents are considerably reduced for the same amalgam concentration.

The following conclusions can be drawn from these observations.

The process of reduction and amalgamation occurs simultaneously. Equation 3, therefore cannot be split up into equations 1 and 2. If it were not the case, then the current values would not have changed with progressively concentrated Cd amalgam cathode, On the contrary, with the exception of cadmium, the current values change considerably even for 0·1% amalgam. It has therefore to be presumed that the forward reaction of equation 3 is retarded when amalgam cathodes are used.

The amalgam cathode does work as a redox indicator electrode in the same way as a simple DME functions in the reduction of non-amalgam forming ions. But the peak potentials and consequently the decomposition potentials are dependent upon the concentration of the amalgam in cathodes. Generally with increasing amalgam concentration, the potentials are shifted towards more negative side, irrespective of their position in the electrochemical series, indicating that the overpotential increases with increasing amalgam concentration. The increasing overpotential essentially results in increasing irreversibility of the electrode reaction with the increasing amalgam concentration, thereby decreasing the polarographic current.

These elements such as copper, zinc which themselves form amalgam with mercury, also give peaks on cadmium amalgam cathode, with the formation of mixed amalgams.

The most noteworthy fact is that cadmium reduction peaks are obtained even for 2% amalgam cathode, with the least dimunition in the current amongst all the other ions tried. A metal amalgam electrode is as good as or even better than the metal electrode itself as an indicator electrode for those metal ions in solution.[13] These results therefore can be explained on these considerations, though the decomposition potentials will be different on mercury and amalgam electrodes.

In the case of other ions, however, the amalgam electrode behaves like the alloy electrode, on the basis of pure mercury being considered as an unalloyed electrode. The efficiency and performance of the platinum electrode which acts as a red-ox and acid-base indicator,[14] markedly deteriorates when alloyed with small amounts of rhodium,[15] due to the increased irreversibility of the electrode processes. In a similar manner, cadmium amalgam efficiency diminishes for the reduction of ions other than cadmium.

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ATOMIC ABSORPTION SPECTROPHOTOMETRY AS A TECHNIQUE IN THE DETERMINATION OF VAPOUR PRESSURE OF METALLIC ELEMENTS

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VAPOUR pressures of a number of metallic elements at various temperatures, measured by different techniques, have been reported by many workers.[1] The vapour pressures of elements like Ag, Au and Mn are extremely low even at flame temperatures, *e.g.*, Ag has a vapour pressure of $9{\cdot}8 \times 10^{-10}$ mm. of Hg at 800° K, Au $3{\cdot}3 \times 10^{-10}$ mm. of Hg at 1000° K. and Mn $3{\cdot}6 \times 10^{-9}$ mm. at 800° K.

In this note, we indicate the applicability of the new technique of atomic absorption spectrophotometry (AAS) in the determinations of vapour pressures of elements like Hg, Ag, Au and Mn at different temperatures.

In the low vapour pressure range under consideration, the partial pressures obey the gas law, *i.e.*,

$$p = n\,k\,T \qquad (1)$$

Absorbance A_T, by the metallic vapour (at temp. T), of the monochromated beam from an HC lamp is proportional to the concentration of atoms '*n*' in the vapour phase. Therefore, we write from eqn.(1):

$$p = K_p.\ A_T T \qquad (2)$$

where K_p is a constant.

The absorbance values at a number of temperatures were obtained for Hg using a quartz window absorption cell having suitable heating and temperature measuring arrangements placed in the path of the monochromated beam (2537 Å) from a Hg vapour lamp. Vapour pressure (p) for Hg at these temperatures was read from standard Tables.[1] Figure 1 gives the results at various temperatures where the linearity of p *vs.* $A_T T$ envisaged in eqn. (2) has been obtained.

Using the Clausius-Clapeyron's equation on variation of vapour pressure with temperature one derives the first approximate relation,

$$\log\ p = \alpha + \beta/T \qquad (3)$$

where α and β are constants characterising the element in a given phase, *i.e.*, log p and 1/T bear a linear relationship. Such relationships for the elements Hg, Ag, Au and Mn have been established by earlier workers at elevated temperatures (900–1000° K.). Combining equations (2) and (3) one obtains:

$$\log\ K_p.A_T T = \alpha + \beta/T$$

or

$$\log\ A_T T = \alpha - \log\ K_p + \beta/T \qquad (4)$$

i.e., log $A_T T$ should bear a linear relationship with 1/T in AAS measurements in the temperature range where the stipulation in relation (3) is valid.

A series of experiments were carried out in the temperature range of 350–1000° K. Metals Ag, Au and Mn used in the experiment were the specpure metals (Johnson and Mathey). These were placed respectively in the absorption cell as above. The cell chambers were flushed with argon then filled with the same to nearly atmospheric pressure and electrically heated to desired temperatures. Prior to taking readings on temperature and absorbance from the respective HC lamps, the argon gas flow was stopped for sometime in order to allow for the attainment of saturation vapour pressure. The linearity as envisaged in relation (4) is obtained in the lower ranges of the temperature for the metals Ag (3281 Å), Au (2428 Å) and Mn (2798 Å). The slopes are found to change in