Anodic Stripping Voltammetry in Propylene Carbonate

R. S. CHITRE, M. M. MEHTA, K. A. KHASGIWALE AND M. SUNDARESAN
Analytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay-400 085

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THE method of anodic stripping voltammetry in an aprotic solvent, viz., propylene carbonate has been applied to the analytical determination of Cu^{++}, Pb^{++}, Eu^{++} etc. using tetraethyl ammonium perchlorate as the supporting electrolyte. The fabrication of the apparatus and the hanging mercury drop electrode has been detailed together with the standardisation of the method and the calibration of the apparatus. Results have been discussed with reference to the peak current and potentials.

ANODIC stripping voltammetry, popularly known as stripping analysis, is a well known electroanalytical method for the determination of elements in trace quantities. While extensive work and numerous applications of this method in aqueous medium are available in literature[1], only scanty data are available in the application of this method in non-aqueous media. Many workers have studied the theory of voltammetric techniques with a linear voltage sweep and many later techniques[2-6] like phase selective anodic stripping voltammetry have increased the sensitivity of this method.

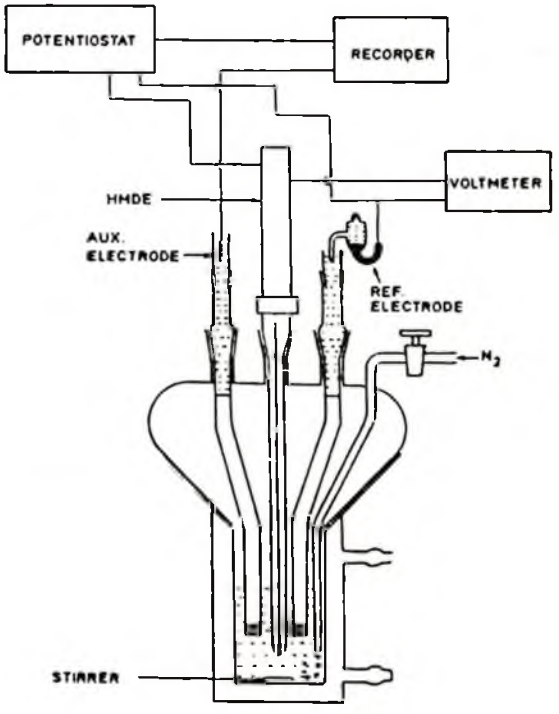
EXPERIMENTAL

A schematic diagram of the apparatus employed in this work is given in Fig. 1. The basic circuit of Santhanam[7], where valves have been replaced with operational amplifiers, was adopted and is given in Fig. 2. The circuit consists of a potentiostat capable of giving constant voltage in the range of +1 to −2.5 volts with a variation of less than 10mV and voltage sweep rate of 1.0 to 10.0 V/min. The three electrode system consisted of (a) Hanging Mercury Drop Electrode (HMDE) giving tenacious mercury drop of areas ranging from 0.01 to 0.1 $mm^2 \pm 0.001$ mm^2 by turning the calibrated micrometer screw. (b) an auxiliary electrode of short platinum wire and (c) saturated calomel electrode with non-aqueous bridge as reference electrode.

Purification of propylene carbonate, preparation of salts like tetraethyl ammonium perchlorate and non aqueous bridge have been already described in our earlier work[8]. The standardisation of the potentiostat voltage sweep apparatus was done in the usual way.

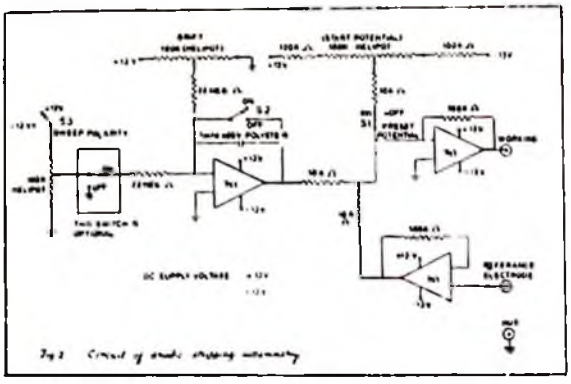
Fig 1

Stripping Voltammetry Apparatus



The following process was followed: The solution under test was deaerated for 15 mins. by purging purified and equilibrated inert gas. Stirring was started and gas bubbling stopped. A fine mercury drop of desired area was pushed out by turning micrometer screw. The chosen value of voltage for constant potential electrolysis E_d was set. Similarly the desired voltage sweep rate was also adjusted on the voltage sweep part. The voltage recorder and current voltage curve recorder were also started.

The pre electrolysis was started by impressing the potential and simultaneously starting the time counting, and was carried out for a desired short period, T_E say 30 secs. at the end of which only the stirring was stopped. A rest time of 30 secs T_R was allowed for solutions to become quiescent.



After the rest time the voltage sweep was started at a definite rate. The current-potential curve showing peaks was recorded. The peak height I_p and peak-voltage E_p were measured. Its width and other parameters are measured. For a new trial the old Hg drop was dismissed by knocking it off and a fresh drop was taken. The whole experiment was repeated as before. A procedural blank was carried out exactly on the same lines excepting the metal ion only.

The apparatus was calibrated using standard aqueous cadmium solution and after ascertaining the satisfactory working of the apparatus, the apparatus was used for anodic srripping voltammetry in Propylene Carbonate (PC).

Table 1 gives the summary of the results obtained with cadmium, lead and europium present as perchlorates. The mean of 3 or more experiments was taken in each case Precautions were taken to see that the salts were dehydrated. Fig. 3 gives a typical anodic stripping curve of cadmium with a concentration of 1.5μg/ml.

DISCUSSIONS

The characterisation of propylene carbonate medium for stripping analysis showed that the observations and conclusions made for chronopotentiometry[11] are valid in this case too. The

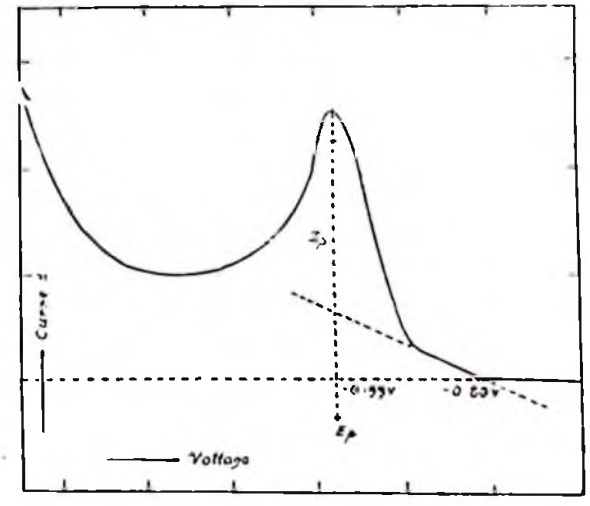
TABLE 1

Values of peak current against metal Concentration in PC

Voltage sweep rate	40 mV/Sec
Area of mercury drop	1.28±0.04mm²
Stirring speed	800 r.p.m.
Supporting electrolyte	0.2 M TEAP
Electrolysis and rest time	30 sec.

Metal	Pre electrolysis Pontential —V *vs* SCE	Concen. μg/ml	I_p nanoamps	Mean I_p	I_p nanoamps/ μg/ml
Cd	—0.8	0.5	24,27,22	24.3	48.6
		1.0	50,47 46	47.6	47.6
		1.5	71,65,70	68.7	45.8
Pb	—0.8	0.5	33,36,42	37.7	75.3
		1.0	69,75,77	73.7	73.7
Eu	2.0	10	13,14,14	13.7	1.37
		50	70,66,68	68.0	1.36
		100	140,131,135	135.3	1.35

Fig 3



Anodic Stripping Curve
Cd^{++} = 1.5μg/ml
Supporting electrolyte = 0.2 M TEAP
Volume = 25 ml
Size of the electrode = 1.28 ± 0.04 mm²
Pre-electrolysis potential = -0.8 V vs SCE
Electrolysis time = 30 secs
Rest time = 30 secs
Stirring speed = 800 r p m
Voltage sweep rate = 40 mV/sec

linear relationship between peak current and concentrations of the ions reveals that this medium will be extremely useful for the analytical determination of elements which are difficultly reducible in aqueous media and cases where hydrogen evolution interferes. This one could sefely work in ranges upto −2.5 V vs SCE in propylene carbonate medium anodic stripping voltammetry.

The peak potential is given by the equation[9].

$$E_p - E_{\frac{1}{2}} = 1.1 \frac{RT}{nF} \qquad (1)$$

where $E_{\frac{1}{2}}$ is the half wave potential. In the case of cadmium the peak potential falls at, as can be seen from Fig. 3 −0.530 vs SCE. The half wave potential of cadmium as given by Gutman[10] is −0.11 V vs SCE where the $E_{\tau/4}$ value obtained by Chitre et al is −0.490 V vs SCE. In view of the fact that the $E_{\frac{1}{2}}$ values obtained by Gutman are vitiated by the fact that an aqueous salt bridge has been used, $E_{\tau/4}$ value obtained by Chitre et al be considered to be equal to $E_{\frac{1}{2}}$.

Thus

$$E_p = -0.490 - 1.1 \times \frac{0.059}{2}$$
$$= -0.490 - 0.033$$
$$= -0.523 \text{ V vs SCE.}$$

This value coincides with the value of peak potential of −0.530 V vs SCE obtained in this paper. In the case of lead also this agreement is noticed.

It may be mentioned that Gutman[10] had attempted stripping voltammetry of europium in propylene carbonate. In fact he has not mentioned anything about the linear relationship with concentration on the conditions of the experiment. The peak potential mentioned by him occured at −1.10 vs SCE while that obtained by us was at −0.70 V vs. SCE. Gutman's value does not correspond to the theoretical value. This divergence is a point worthy of investigation.

It was found that Cd^{++} and Pb^{++} ions individually gave reproducible peaks (Table 1) but in mixtures of the two the peaks overlapped and resolutions became difficult for analytical purposes. This might be due to probable formation of intermediate compounds of Cd and Pb on the mercury surface or due to oxidations and reductions. If this is so, then, perhaps, the problem could be solved by mixing other aprotic solvents with propylene carbonate. The diffusion coefficients of cadmium and lead in propylene carbonate vary by an order of 10 from the respective coefficents in mercury[11]. The divergence in this result must have to be examined in detail taking into consideration the particular influence of moisture in the solvent.

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