

The unusual potentiometric behaviour of bromine and its application in the estimation of some substrates

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The uncatalysed bromate system involving acid, bromate and a substrate has been studied in detail. The related stationary potential measurements show an unusual behaviour of bromine at a critical concentration. This is made use of in the estimation of a large number of water soluble as well as water insoluble substrates at a concentration level of $10^{-4}M$. The large amplitude oscillations in the uncatalysed bromate system are due to the response of the indicator electrode to two different redox systems involving bromine.

The uncatalysed bromate oscillator involving bromate, acid and a substrate has been studied by employing different substituted aromatic compounds¹⁻⁶. The key role played by the variation in potential with [bromine] around a critical value has been taken advantage of in the estimation of several compounds in aqueous medium at a concentration level of $10^{-4} M$ (ref. 7).

The low solubility of many compounds in aqueous medium was an impediment in employing them as substrates in the oscillatory system. Moreover, they could not be estimated by the potentiometric method. The use of mixed media containing various percentages of organic solvents enabled the study of a large number of new substrates in the iodate-hydrogen peroxide system as well as the bromate systems, both catalysed and uncatalysed⁸⁻¹¹. The present paper deals with the potentiometric estimation of several substrates at a concentration level of about $10^{-4} M$ in aqueous as well as in mixed media. In the mixed medium, the organic solvent is the minor constituent and is present to the extent of less than 0.2% (by volume).

Experimental

All the chemicals used were of AnalaR grade purity and used without further purification. Doubly distilled water was used for preparing all the solutions. Experiments were carried out in a pyrex

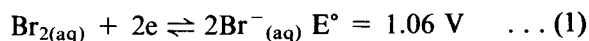
glass vessel of about 30 ml capacity into which a platinum indicator electrode and a potassium nitrate salt bridge were introduced. The total volume of the reaction mixture, which was $10^{-4} M$ in potassium bromide, $10^{-1} M$ in sulphuric acid and $2 \times 10^{-5} M$ in bromine (so as to give a potential value of ~ 850 mV) was kept at 25 ml. The reaction mixture, thermostated at $30 \pm 0.1^\circ C$, was kept stirred using a magnetic paddle. The emf of the cell was measured using a digital multimeter HIL 2103 by coupling the platinum indicator electrode to a saturated calomel electrode (SCE) through the potassium nitrate salt bridge.

Bromine was dissolved in water to get a saturated solution, standardised iodometrically and diluted successively to get the required concentration.

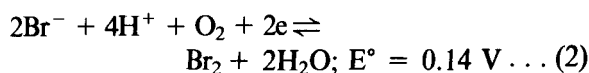
In the case of water soluble substrates, a solution of $10^{-1} M$ was prepared in doubly distilled water. Then by successive dilution, a solution of $10^{-4} M$ was prepared. For water insoluble compounds, a concentrated solution ($10^{-2} M$) of the substrate was prepared in water-acetonitrile mixture and a $10^{-4} M$ solution was obtained by successive dilution with doubly distilled water. The reaction mixture contains less than 0.2% (v/v) acetonitrile.

Results and discussion

Stationary potential measurements were carried out in aqueous as well as mixed media containing different percentages of acetonitrile. The plots of $-\log [Br_2]$ against the potential are presented in Fig. 1. The plots are characterised by a sharp increase in potential by several hundred millivolts for a small change in [bromine]. Such an increase is observed at a critical [bromine]. The high potential region (~ 850 mV) in the curve is identified with the redox reaction,



As [bromine] decreases, there is a sudden downward jump in the potential leading to a linear variation of potential with [bromine]. This part of the curve is presumably due to the reaction.



Stationary potential measurements with deaerated solution decreased the lower potential

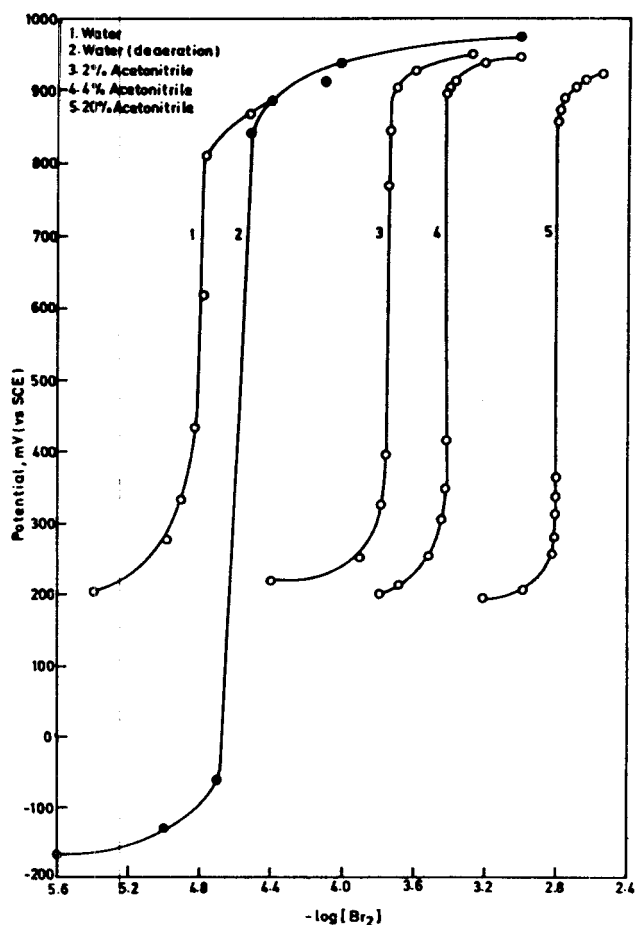


Fig. 1—Plot of potential against $-\log [\text{Br}_2]$

region by about 300 mV (Fig. 1). Stationary potential values obtained independently with different [bromide] and [sulphuric acid] confirm that the potential in this region is caused by acidified bromide. The large amplitude oscillations in the uncatalysed bromate oscillators are due to the fact that the indicator electrode senses the potential of the redox systems involving bromine. The potential corresponds to the bromine-bromide redox reaction (Eq. 1) when [bromine] is above the critical value ($2 \times 10^{-5} M$). At lower [bromine], the electrode is responsive to the redox reaction involving oxygen (Eq. 2). This causes a sudden potential drop in the plot of potential versus $-\log [\text{Br}_2]$.

The critical [bromine] at which the potential jump occurs shifts to a higher value with the increase in the percentage of acetonitrile (Fig. 1). This is a consequence of the interaction between acetonitrile and bromine resulting in a lowering of concentration of free bromine. The concentration of free bromine alone is sensed by the platinum indicator electrode.

Table 1—Spectrophotometric data

$[\text{KBr}] = 10^{-4} M$; $[\text{Br}_2] \times 10^3$ M	$[\text{H}^+] = 10^{-1} M$ ($\lambda = 460 \text{ nm}$) Optical density	
	Aqueous medium	Acetonitrile 20% (volume)
2.5	0.35	0.20
5.0	0.75	0.56
7.5	1.13	1.05
10.0	1.70	1.60

Spectrophotometric measurements with different concentrations of bromine in aqueous as well as in mixed medium established such an interaction between bromine and the organic solvent. The optical density values in the two media are given in Table 1.

In the presence of bromide ion, bromine would undergo complex formation according to the reaction,



The equilibrium constant value for the above reaction in pure aqueous medium is ~ 16 at 25°C , whereas its value is $\sim 10^7$ in pure acetonitrile¹². This clearly shows that the equilibrium constant for the formation of Br_3^- ion in 20% (v/v) acetonitrile-water mixed medium would be higher than that in pure aqueous medium (about 250 obtained by interpolation), thereby reducing the concentration of free bromine (in 20% acetonitrile) with corresponding decrease in the electrode potential and optical density.

The solution of the compound to be estimated ($\sim 10^{-4} M$) is added in small volumes from a microburette into the reaction mixture and the corresponding potentials were noted. The potential gradually decreases from an initial value of ~ 850 mV (vs SCE) after each addition of the solution of the substance to be estimated. The volume beyond which there is a less steep decrease in the potential (~ 250 mV) represents the attainment of equivalence point. This is obtained by the inflection method as in usual potentiometric titrations.

The method has been successfully employed for the estimation of substituted aromatic compounds, flavones and some inorganic substances. Several of these compounds are not soluble in aqueous medium. In most of the cases, the results are found to be correct within the limits of $\pm 5\%$. The technique is being extended for the estimation of other classes of compounds employing aqueous-acetonitrile as well as other mixed media.

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