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Polarography of Some Anions in Aqueous Organic Solvent Mixtures

Part II

Reduction of Iodate Ions in Aqueous Mixtures of Methanol, Ethanol, n-Propanol, iso-Propanol, Ethylene Glycol, Propylene Glycol, 1,2-Propanediol and Glycerol

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The present investigation deals with the polarographic behaviour of iodate ions in various aqueous mixtures of methanol, ethanol, n-propanol, iso-propanol, 1,2-propanediol, 1,3-propanediol, and glycerol at 30 °C. $0.1M$-NaOH was used as a base electrolyte. The half-wave potential ranges from 1.24 to 1.46 and the diffusion current decreases with increasing percentage of the solvent. The plots of i_d vs. $\sqrt{h}$ and i_d vs. c were linear and pass through origin for all the solvent mixtures, showing that the limiting current is diffusion controlled. The plots of $\log i/(i_d - i)$ vs. $E_{d.e.}$ were linear for all the aqueous organic solvent mixtures, but the value of slope suggested that the reductions are irreversible. The electrode kinetics was studied by *Koutecky*'s method for irreversible electrode process.

The reduction of iodate and bromate ions was studied by *Rylich*[1] in aqueous media at dropping mercury electrode and reported similar results for both anions. Little attention has been paid so far towards the reduction of anions in aqueous, non-aqueous and aqueous—non aqueous solvent mixtures. Recently we have studied the reduction of chromate[2], bromate[3], and iodate[4] ions in presence of various type of indifferent electrolytes in aqueous media. The reduction of chromate[5-7] and bromate[8, 9] ions in various aqueous organic solvent mixtures have also been investigated by the authors. The present paper deals with the polarographic behaviour of iodate ions in aqueous mixtures of methanol, ethanol, n-propanol, iso-propanol, propylene glycol, 1,3-propanediol and glycerol.

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Experimental

Polarograms were obtained on a manual set up. The applied voltage was checked by Pye vernier potentiometer. The polarized electrode has the following characteristics: $m = 1.146$ mg/sec and $t = 5.1$ sec (in $0.1M$-NaOH at — 1.0 V vs. *SCE*) was used for all the measurements.

All the chemicals used were of reagent grade purity. The stock solutions of IO_3^- ($0.01M$) and NaOH ($1.0M$) were prepared in doubly distilled water and standardized. All the solvents were purified and distilled by standard methods. The suitability of the solvent for polarographic work was tested by blank polarograms of solvent having $0.1M$-NaOH. The viscosity and density of the solutions were measured by Ostwald viscometer and pyknometer respectively.

1 mM-IO_3^- and $0.1M$-NaOH solutions with different percentage of the solvent (by volume) were prepared as usual. No maxima suppressor was added as maximum does not appear. Solutions having different concentration of IO_3^- and $0.1M$-NaOH were also prepared in same percentage of the solvent. The electrolysis was carried out after deaeration with purified N_2 presaturated with the given solvent mixtures in a H type cell. All the measurements were carried out at 30 °C which was controlled by Haake type ultrathermostat. The IR drop correction was applied wherever needed. For this purpose LP conduscope was used to measure the circuit resistance.

Results and Discussion

Polarograms were obtained manually in 10, 20, 40, and 60% (by volume) of ethanol, n-propanol, iso-propanol, propylene glycol and glycerol. At the higher percentage of these solvents layer formation takes place, thus the resistance increases which diminishes the current considerably.

For all other three solvents, experiments were performed up to 80%. All the solutions produce single well defined wave. The half wave potentials were determined from the intercept of the plots of log $i/i_d—i$ vs. $E_{d\cdot e\cdot}$, which were linear in all cases. For all the solutions, the half-wave potential ranges from — 1.24 V to — 1.46 V vs. *SCE*. The slope of these plots was much higher than that needed for six electron reversible reduction (10 mV at 30 °C). Furthermore, the plots of i_d vs. $\sqrt{h}$ (h = effective height of mercury column) and plots of i_d vs. C (concentration of IO_3^-) were linear and pass through origin. The above results conclude that although the current is limited by diffusion for reduction of IO_3^- but the electrode process is highly irreversible.

The values of D (diffusion coefficient) for IO_3^- in all the organic aqueous solvent mixtures have been calculated by *Ilković* equation and it was found that the diffusion coefficient of IO_3^- decreases with the increasing proportions of the organic solvents, which is due to the increasing viscosity of the mixtures. The value of D in aqueous media (0.1 M-KCl) comes to 1.05×10^{-5} cm$^2\cdot$s^{-1} which is in agreement with the value calculated by *Kolthoff* and *Lingane*[10] (1.09×10^{-5} cm$^2\cdot$s^{-1}).

Table 1. *Polarographic characteristics and kinetic parameters for the* IO_3^- *(1 mM) in different aqueous organic solvent mixtures at 30 °C*

S. No.	Solvent	Percentage (by Volume)	i_d (μ A)	$E_{1/2}$ (—V vs. S.C.E.)	$D^{1/2} \cdot 10^3$ (cm²/sec)	K^0_{fh} (cm/sec)	α_n
1.	Methanol	10	16.00	1.340	3.25	6.31×10^{-14}	0.65
		20	14.75	1.350	3.00	1.12×10^{-15}	0.66
		40	13.25	1.404	2.69	1.58×10^{-15}	0.72
		60	12.75	1.269	2.59	7.94×10^{-16}	0.74
		80	13.50	1.370	2.75	1.26×10^{-17}	0.75
2.	Ethanol	10	14.75	1.350	3.00	6.31×10^{-16}	0.75
		20	13.25	1.440	2.69	7.94×10^{-17}	0.79
		40	12.00	1.412	2.44	1.99×10^{-18}	0.78
		60	10.50	1.377	2.13	4.47×10^{-17}	0.80
3.	n-Propanol	10	15.50	1.376	3.15	7.94×10^{-16}	0.73
		20	14.00	1.408	2.85	1.99×10^{-17}	0.76
		40	11.75	1.368	2.39	1.26×10^{-19}	0.86
		60	8.25	1.319	1.68	1.26×10^{-21}	0.97
4.	Iso-propanol	10	7.50	1.248	1.52	1.00×10^{-8}	0.30
		20	10.00	1.430	2.03	7.08×10^{-8}	0.31
		40	14.00	1.460	2.85	1.59×10^{-9}	8.30
		60	29.00	1.460	5.90	1.00×10^{-10}	0.30
5.	Ethylene-glycol	10	14.54	1.300	2.96	1.00×10^{-12}	0.52
		20	12.65	1.310	2.57	1.59×10^{-9}	0.33
		40	9.81	1.315	1.99	1.78×10^{-9}	0.35
		60	7.55	1.320	1.54	5.62×10^{-9}	0.40
		80	5.94	1.310	1.21	1.41×10^{-11}	0.49
6.	1 : 2 Propane-diol	10	15.30	1.370	3.11	8.91×10^{-10}	0.46
		20	12.08	1.290	2.46	2.51×10^{-12}	0.54
		40	9.06	1.297	1.84	1.11×10^{-13}	0.60
		60	7.65	1.310	1.56	3.98×10^{-12}	0.65
7.	1 : 3 Propane-diol	10	15.30	1.370	3.11	8.91×10^{-12}	0.54
		20	13.21	1.350	2.69	2.81×10^{-13}	0.54
		40	13.12	1.310	2.69	4.47×10^{-8}	0.35
		60	10.95	1.290	2.23	3.98×10^{-7}	0.29
		80	7.74	1.300	1.58	6.31×10^{-6}	0.25
8.	Glycerol	10	12.70	1.250	2.58	6.31×10^{-14}	0.72
		20	12.10	1.250	2.46	2.51×10^{-15}	0.77
		40	7.94	1.240	1.62	5.62×10^{-15}	0.81
		60	4.81	1.240	0.98	5.62×10^{-14}	0.77
9.	Water		16.50	1.270	3.36	3.98×10^{-14}	0.64

As the reductions are highly irreversible, the kinetics of the electrode process was studied by *Koutecky*'s method. The kinetic parameters K^0_{fh} and α_n (transfer coefficient) were calculated as discussed earlier[3]. The plots of $-\log K_{fh}$ vs. E (—V vs. *NHE*) were linear for all the solutions. The extrapolation of these plots to the standard hydrogen potential, i.e. zero volt gave the values of K^0_{fh} whereas α_n was obtained from the slope of these plots. The $K_s{}^0$ (standard rate constant) could not be obtained for such systems, as the value of the standard electrode potential is not known in these aqueous organic solvent mixtures. The kinetic parameters and polarographic characteristics for reduction of OI_3^- in various aqueous organic solvents are summarized in Table 1.

As there is no significant change in polarographic characteristics and α_n with addition of organic solvent to the aqueous solution, so it is probable that there is no change in the mechanism of the electrode reaction. Furthermore, iodate can be estimated in these organic solvent mixtures as the current is limited by diffusion.

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