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Polarography of Various Cations in Acetamide. II. Studies with Nickel(II), Cobalt(II), Manganese(II) and Zinc(II) in Acetamide

S. K. JHA and S. N. SRIVASTAVA

Department of Chemistry, Agra College, Agra, India

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Polarographic behaviours of Ni(II), Co(II), Mn(II) and Zn(II) have been studied in varying concentrations of acetamide in aqueous medium with KCNS as the indifferent electrolyte. Complex formation is noticed in all the cases with an irreversible wave character. αn_a and rate constant (k_{f,h°) have been calculated in the case of Ni(II), Mn(II) and Zn(II). Cobalt gives a dip. The dip is eliminated in the presence of 0.0075% Triton X-100.

A good deal of interest has developed recently in polarographic studies of various electroreducible ions in the presence of organic substances. The studies were confined to a few organic compounds which were appreciably miscible with water. Measurements have been made polarographically in non-aqueous media *viz* acetonitrile, amides, *etc.* by various workers.[1,2] Hale and Parsons[3] have reported their work on Cd(II) in formamide and other substituted amides.

In the present communication, the authors have investigated the polarographic behaviour of the depolarizers Ni(II), Co(II) Mn(II) and Zn(II) in varying concentration of acetamide in aqueous medium, potassium thiocyanate has been used as the indifferent electrolyte in all these cases at ionic strength, $\mu=1.0$.

Experimental

Nickel chloride, cobalt(ous) nitrate, manganese chloride and zinc sulphate were of E. Merck reagent grade. Potassium thiocyanate Analar B. D. H. was used as the indifferent electrolyte. All solutions were prepared in conductivity water.

Current-voltage curves were recorded by means of a manual polarograph (Worsley-Lanc's) in conjuction with a Pye Galvanometer. Mercury for d. m. e. was of high purity. The droptime, t, in the open circuit was found to be 2.612 sec at a constant corrected height of mercury column of 39.6 cm. Deaeration of all the samples was accomplished by passing purified[4] hydrogen generated in Kipp's apparatus. Polarographic half cell was connected through an agar-bridge (saturated with NH_4NO_3) to the saturated calomel electrode γ (SCE). All measurements were perforemed at 25 ± 0.1°C.

The concentration of the depolarizer in all the case was taken 5×10^{-4} M in the presence of 1 M KCNS. Gelatin (0.01%) was used as the maximum suppressor. The percentage of acetamide (by weight) was varied from 0 to 30%.

Results

On applying the different criteria of reversibility it was found that the process was irreversible in case of all the depolarizers. Thus the usual equation for a reversible polarographic process seemed to be untenable for the analysis of data.

Meites and Israel[5] have shown in their treatment for irreversible waves

$$E = E' - \frac{0.0542}{\alpha n_a}\left[\log\frac{i}{i_d-i} - 0.546\log t\right] \quad (1)$$

where

$$E' = \frac{0.05915}{\alpha n_a}\log\frac{1.349\,k_{t,\,h^\circ}}{D_0^{1/2}} \quad (2)$$

The value of αn_a is best obtained from the slope of a plot of E *versus* $[\log(i/i_d-i)-0.546\log t]$; according to Eq. (1), this slope is equal to $-(0.0542/\alpha n_a)$ V. The intercept of the same plot, which is equal to E' can then be used to calculate k_{f,h° by means of Eq. (2) with the aid of an estimate of D_0.

The magnitude of D_0 is determinable from the relation

$$D_0 = \frac{RT}{F^2}\times\frac{\lambda^0}{z}$$

Since cations Ni(II), Co(II), Mn(II) and Zn(II) posses the same ionic radii approximately, the value of (λ_0/z) for all the ions[6] is ≈26.5

$$D_0 = 2.67\times10^{-7}\times\frac{\lambda^0}{z}\ \text{cm}^2/\text{sec at } 25^\circ\text{C}$$

1) G. H. Brown and H. Hsiung, *J. Electrochem. Soc.*, **107**, 57 (1960).
2) R. C. Larson and R. T. Iwamoto, *J. Am. Chem. Soc.*, **82**, 3239 (1960).
3) J. M. Hale and R. Parsons, Advan. Polarog., Proc. Intern. Congr., 2nd, Cambridge, England, 1959, 3829—3839 (Pub. 1960).
4) L. Meites, "Polarographic Techniques," Interscience Publisheres, Inc., New York (1955), p. 33.
5) L. Meites and Y. Israel, *J. Am. Chem. Soc.*, **83**, 4903 (1961).
6) L. Meites, "Polarographic Techniques," Interscience Publisheres, Inc., New York (1965), p. 144.

Table 1. Polarographic characteristics

't' 2.612 sec, '$m^{2/3}t^{1/6}$' 1.962 'm' 2.237 mg

Percentage of acetamide	$E_{1/2}$, V *vs.* SCE	Slope	αn_a	$k_{f,h}°$
		Zn		
5	−1.560	0.1195	0.4535	3.653×10^{-18}
10	−1.584	0.1375	0.3942	1.421×10^{-17}
15	−1.600	0.1395	0.3888	1.326×10^{-17}
20	−1.614	0.1428	0.3796	8.966×10^{-16}
25	−1.640	0.1466	0.3697	6.960×10^{-16}
30	−1.660	0.1507	0.3596	6.203×10^{-16}
		Mn		
5	−1.630	0.0869	0.6237	5.924×10^{-23}
10	−1.653	0.0990	0.5475	7.991×10^{-21}
15	−1.680	0.1087	0.4985	5.7989×10^{-20}
20	−1.696	0.1190	0.4555	4.598×10^{-19}
25	−1.734	0.1333	0.4065	3.256×10^{-18}
30	−1.747	0.1407	0.3853	9.607×10^{-17}
		Ni		
5	−1.562	0.1042	0.5202	2.201×10^{-20}
10	−1.587	0.1111	0.4878	4.927×10^{-19}
15	−1.604	0.1162	0.4663	1.788×10^{-19}
20	−1.631	0.1280	0.4235	1.917×10^{-18}
25	−1.640	0.1305	0.4153	1.296×10^{-18}
30	−1.648	0.1333	0.4065	8.762×10^{-17}

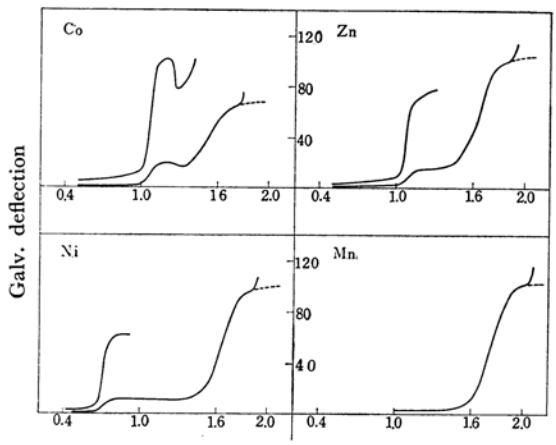

Fig. 1. Polarograms of the various cations (5×10^{-4}) in presence of 15% acetamide, 1 M KCNS and 0.1% gelatin.

Nickel, cobalt and zinc yield two waves in KCNS-acetamide solutions. The first wave (a) in all the three cases represents metal ion-KCNS electroreduction while the second wave (b) is a composite wave of the above referred reduction as well as metal ion-acetamide reduction at a lower sensitivity. The composite wave could not be recorded at the sensitivity of the first wave. Mn(II) yields only one wave.

The following results have been computed by making use of the above equations.

Zinc Ion as Depolarizer. Normally, zinc yields a single, well defined and diffusion controlled wave in presence of 1 M KCNS with $E_{1/2}=-1.055$ V *vs.* SCE. In presence of acetamide in varying concentrations from 0 to 30% and 1 M KCNS, it gives a double wave (Fig. 1). The first wave is obviously due to the reduction of simple ion to the metal. The $E_{1/2}$ of the first wave is almost constant and ranges from −1.04 to −1.08 V *vs.* SCE. The second wave presumably is owing to the reduction of zinc-acetamide complex and the complex is evidently reduced at a higher negative potential. The occurrence of complex formation[7] is quite evident because of a measurable shift in $E_{1/2}$. Slope determinations from plots of E *vs.* $\log i/(i_d-i)$ and $E_{3/4}-E_{1/4}$ show that the second wave which seems to be due to the reduction of the complex is highly irreversible. Calculations for factors αn_a and $k_{f,h}°$ show that the transfer coefficient decreases with the increase in acetamide content while $k_{f,h}°$ increase with the increment in acetamide concentration. The increase in $k_{f,h}°$ shows the tendency of the wave towards reversibility although value lower than 3×10^{-5} cm/sec bears testimony to an irreversible process.[8]

Manganese Ion as Depolarizer. According to Kolthoff[9] a well-defined Mn(II) wave is obtained in 1 M KCNS in presence of 0.01% gelatin with $E_{1/2}=-1.55$ V *vs.* SCE. But in the present work no well-formed wave under identical conditions is obtained; rather the wave is drawn out (Fig. 2). However, in the presence of acetamide, well defined wave can be obtained which can prove useful in estimation of the cation with greater precision in usual practice. The reaction is irreversible and $E_{1/2}$ is shifted to a more negative potential showing thereby complex formation with the acetamide. Only a single wave is obtained.

Nickel Ion as Depolarizer. Nickel in the presence of 1 M KCNS (as indifferent electrolyte) gives a fairly well defined wave with $E_{1/2}=-0.695$ *vs.* SCE. In the presence of acetamide a double wave (Fig. 1) is exhibited. The two waves are widely separated. The first wave is due to the reduction of thiocyanate complex of nickelous ion, which is already reported in literature. The other wave which is obtained at a higher negative potential is owing to the reduction of nickel acetamide complex. The behaviour of the second wave is highly irreversible. For an irreversible reduction of a complex at d. m. e, the rate of formation and dissociation of certain complex

7) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, Interscience Publisheres, Inc., New York (1965), p. 211.
8) Ref. 5, p. 236.
9) Ref. 6, Vol. II, p. 469.

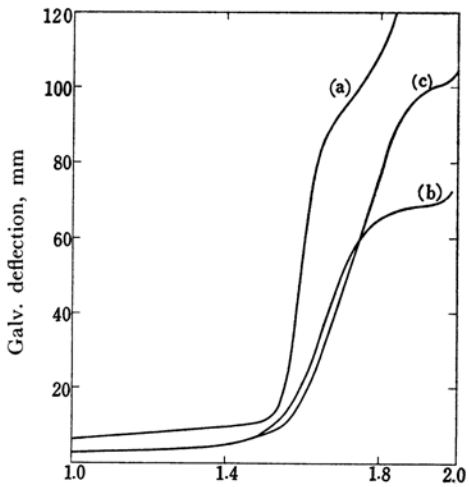

Fig. 2. Polarograms of Mn(II), 5×10^{-4} M, in 1M KCNS, 0.01% gelatin and (a) 0%, (b) 15% and (c) 30% acetamide.

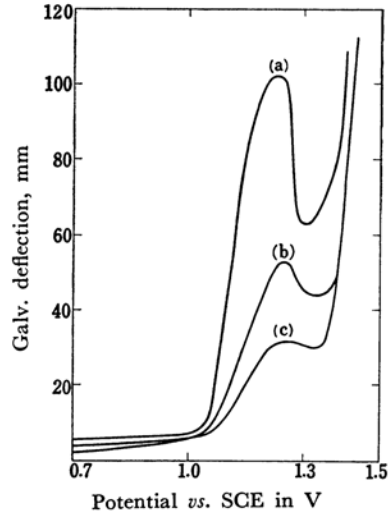

Fig. 3. Polarograms of Cobalt(II), 5×10^{-4} M, in 1 M KCNS and (a) 0.0025%, (b) 0.0050% and (c) 0.0075% Triton X-100.

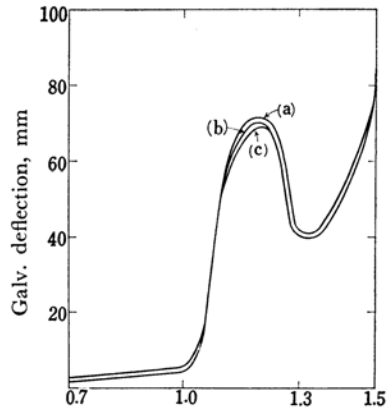

Fig. 4. Effect of camphor (a) 0.0025%, (b) 0.0050% and (c) 0.0075% on the polarograms of cobalt(II).

metal ions is often quite slow. Thus in reduction of such complexes at d. m. e., certain other polarization effects in addition to concentration polarization may come into play. In such cases, the equation of the wave invalves the rate constant of the slow step in the electrode reaction. Since satisfactory quantitative interpretation of irreversible waves is not available,[10] the analysis has been done with the equation already given in the beginning of the paper.

Cobalt Ion as Depolarizer. In neutral thiocyanate solutions the diffusion current is well defined when gelatin is present.[11] However in slightly acid thiocyanate solutions the diffusion current shows a peculiar minimum even in the presence of gelatin which makes it unsuitable for analytical purposes. An analogous case in hexamminecobalt(III) has been met with by I. M. Kolthoff and Khalafalla.[12] In the present work Co(II) also gives a wave with a hump in the wave range of -1.1 to -1.2 V *vs.* SCE; with a further increase in voltage (-1.25 to -1.30 V *vs.* SCE) a dip is observed. The cumulative pH of the solution is 4.9. A second wave (Fig. 1) which follows the dip is due to the complex formation as in the case of nickel. Since the diffusion current is not well-defined because of the occurrence of dip, no quantitative treatment can be made for the second wave.

An attempt has been made to study the effect of varying amounts of gelatin, Triton X-100 and camphor (Fig. 4) on the polarograms of Co(II). The former two affect the diffusion current considerably with the depression in wave height. At a concentration of 0.0075% of Triton X-100, the dip is more or less eliminated. Effect of various concentrations of Triton X-100 on diffusion current and magnitude of the dip are given in (Fig. 3).

Thus cobalt shows an anomalous behaviour in so far as it gives a dip in the wave which could not be removed to the extent amenable to mathematical treatment. However for nickel, manganese and zinc the following generallizations could be made.

(i) The $E_{1/2}$ gets shifted to a more negative potential; this proves complex formation with acetamide.

10) Ref. 6, p. 234.
11) Ref. 6, p. 484.
12) I. M. Kolthoff and S. E. Khalafalla, "Review of Polarography" (Japan), Vol. II (1963).

(ii) αn_a decreases regularly in these cases.

(iii) All the cations are irreversibly reduced and with the increasing percentage of acetamide, the rate constant k_{f,h° increases in all the cases.

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