# Polarography of Various Cations in Formamide – Studies with Ni(II), Co(II), Mn(II) and Zn(II)

By S. K. Jha and S. N. Srivastava

## Summary

Polarographic behaviour of Ni(II), Co(II), Mn(II) and Zn(II) has been studied in varying concentration of formamide in aqueous medium with Sodium Perchlorate as the indifferent electrolyte. A decrease in diffusion current, "$i_d$" and diffusion coefficient, "D" is noticed. The ionic radius, "r" is found increasing with increasing percentage of formamide. These three factors coupled with inconstancy in "$i_{d_\eta^{1/2}}$" show that solvation is of major importance in influencing the various parameters of the Ilkovic Equation. Except for Mn(II) all reductions are found to be of irreversible character. "$\alpha_{na}$" and rate constant "$K_{t,h^\circ}$" have been calculated.

## Introduction

The present communication is in continuation with the paper already accepted for publication in The Bulletin of the Chemical Society of Japan[1]). Polarographic studies both in aqueous and non-aqueous media fo these ions have been reported in recent years. Jain and Gaur[2]) have studied polarography of Mn(II) in aqueous mixture of alcohols. Brown and Hsiao Shu Hsiung[3]) have reported "$E_{1/2}$" of various cations including all the four under reference in purely non-aqueous formamide solutions. Hale and Parsons[4]) have reported work on Cd(II), Pb(II) and Tl(I) in both purely non-aqueous formamide and other substituted amides as well as in their aqueous mixtures. Measurements have also been made polarographically in other non-aqueous media viz acetonitrite, amides etc. by various workers[3])[5]). However, as obvious the studies in aqueous mixtures have been confined to solvents which are sufficiently miscible with water.

[1]) S. K. Jha and S. N. Srivastava, Bull. chem. Soc. Japan Accepted for Publication.

[2]) D. S. Jain and J. N. Gaur, Acta. Chim. Acad. Sci. Hung. 42 (1), 7 (1964) (Eng.).

[3]) H. Brown and Hsiao Shu Hsiung, J. Electro Chem. Soc. 107, 57 (1960).

[4]) J. M. Hale and R. Parsons, Advan. Polarography, Proc. Intern. Congress, 2nd, Cambridge, Engl. 1959, 3, 829 [pub. (1960)].

[5]) R. C. Larson and T. Twamots, J. Amer. chem. Soc. 82, 3239 (1960).

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

## Experimental

Nickel chloride, Cobalt (ous) Nitrate, Mangenese chloride and Zinc sulphate were of E. Merck grade. Sodium Perchlorate Analar B.D.H. was used as indifferent electrolyte. Formamide was also A.R. B.D.H. All solutions were prepared in conductivity water.

Pyrex glass was used in the experimental work. The dropping mercury electrode (d.m.e.) constituted of a standard capillary (E. H. Sargent & Co.) with a drop time 3.38 sec. in the open circuit at a constant mercury pressure of 53.63 cms. A manual polarograph (Worsley-Lancs) in conjuction with a Pye galvanometer was used for measuring potential (E) and current respectively. Deoxygenation of the samples was done by passing steady stream of hydrogen gas purified by the method of MEITES[6]). Since the constituents of the solvent possess different vapour pressures, the gas used for deaeration, was passed through a gas-washing small bottle filled with the mixed solvent before it entered the cell. This presaturation of the gas steam prevented the differential evaporation of one ccmponent which could alter the viscosity of medium thereby causing a change in diffusion coefficient. Potentials were measured versus saturated calomel electrode (S.C.E.). Conductivity water was used in preparation of all solutions. Mercury used for d.m.e. was of high purity. Viscosity determination were made by an OSTWALD's viscometer. The percentage of fromamide (by volume) was varied from 0 to 60%.

## Results

On applying the different criteria of reversibility it was found that the reduction of all the depolarizers except for Mn(II) were irreversible. BROWN and HSIAO SHU HSIUNG had also found the reduction of Mn(II) to be reversible in purely non-aqueous formamide medium. Thus the usual equation for a reversible polarographic process seemed to be untenable for the analysis of the data in case of Zn(II), Ni(II) and Co(II).

MEITES and ISREAL[7]) have shown in their treatment for irreversible waves

$$E = E' - \frac{0.0542}{\alpha_{na}} (\log i/i_{d-i} - 0.546 \log t) \tag{1}$$

where

$$E' = \frac{0.05915}{\alpha_{na}} \log 1.349\, K_{f,h^\circ}. \tag{2}$$

6) L. MEITES, "Polarographic Techniques", Inter Science Publishers, Inc., New York. p. 33 (1955).

7) L. MEITES and Y. ISREAL, J. Amer. chem. Soc. 83, 4903 (1961).

The value of "$\alpha_{na}$" is best obtained from the slope of the plot of E vs. [log $i/i_{d-i}$ — 0.546 log t]; according to equation (1) this slope is equal to — $0.0542/\alpha_{na}$ volts. The intercept of the same plot which is equal to E' can then be used to calculate "$K_{f,h^{0}}$" by means of equation No. 2 with the aid of an estimate of "D", the diffusion coefficient.

Evaluation of slope and $E_{1/2}$ for Mn (II) was done from the equation

$$E_0 = E_{1/2} - \frac{0.0591}{n} \log i/i_{d-1}.  \tag{3}$$

The diffusion coefficient were evaluated from the Ilkovic equation

$$i_d = 607 \, n \, D^{1/2} \, C m^{2/3} t^{1/6},$$

where all the parameters involved have their usual significance.

| | |
|---|---|
| Height of the mercury column | = 53.63 cms. |
| Mass of mercury flowing per sec. "m" | = 3.371 mgs. |
| Drop time "t" in open circuit | = 3.38 sec. |
| Concentration of depolarizer | = 5 · $10^{-4}$ Mol. |
| Sensitivity of galvanometer | = 6 · 8965 · $10^{-8}$ amp/div. |

## Discussion

On examination of table 1 we find that $i_d$ ($\mu$ amps) is maximum in the absence of formamide but it goes on diminishing with the increase in percentage of formamide in all the four cases. Studies on limiting currents suggest that it depends upon the following factors.

1. Changes resulting from the variation of the effective diffusion coefficient of the ion.

2. Viscosity.

3. Ionic strength.

4. Complex formation.

5. Environment effect.

6. Hydrogen over voltage.

In the light of these factors the changes in the limiting currents will be studied. Factors viz ionic strength, hydrogen over voltage do not seem to be operative in our case. The complex formation is also not suggested because variation in $E_{1/2}$ is not to an appreciable extent. Hence the changes met with are directly or in-directly related with diffusion coefficient, viscosity and ion interaction.

Viscosity in centipoise increases with increasing formamide content. Hence an increase in viscosity affects diffusion coefficient ultimately resulting in the depression of $i_d$. In order to test the applicability of STOKE's EINSTEIN equation the value of "$i_{d\eta^{1/2}}$" has been found in each case. Since "$i_{d\eta^{1/2}}$" is not constant, the change in diffusion coefficient D which ultimately affects $i_d$, is not solely due to viscosity changes. The varying values

Table 1

| S.No. | Percentage of formamide by volume | $i_d$ μamps | $E_{1/2}$ Versus S.C.E. | Slope volts | Diffusion Coefficient cm² sec⁻¹ (D) | Ionic Radius ($r \cdot 10^{-10}$ cm) | $i_{d\eta^{1/2}}$ | $\alpha_{na}$ | $K_{f,h}^0$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Zn(II) | | | | |
| 1 | 0 | 6.34 | −1.013 | 0.0537 | $1.443 \cdot 10^{-5}$ | 1.330 | 7.684 | 1.009 | $1.920 \cdot 10^{-15}$ |
| 2 | 7.5 | 5.51 | −1.016 | 0.0500 | $1.091 \cdot 10^{-5}$ | 1.518 | 6.330 | 1.084 | $1,656 \cdot 10^{-15}$ |
| 3 | 15 | 4.68 | −1.021 | 0.0428 | $7.889 \cdot 10^{-6}$ | 1.930 | 5.591 | 1.266 | $1.522 \cdot 10^{-15}$ |
| 4 | 30 | 3.94 | −1.024 | 0.0438 | $5.567 \cdot 10^{-6}$ | 2.350 | 5.086 | 1.237 | $1.308 \cdot 10^{-15}$ |
| 5 | 45 | 3.24 | −1.047 | 0.0390 | $3.763 \cdot 10^{-6}$ | 2.887 | 4.590 | 1.366 | $1.086 \cdot 10^{-15}$ |
| 6 | 60 | 1.93 | −1.077 | 0.0343 | $1.336 \cdot 10^{-6}$ | 6.369 | 3.091 | 1.580 | $8.509 \cdot 10^{-14}$ |
| | | | | | Ni(II) | | | | |
| 1 | 0 | 5.03 | −1.050 | 0.0834 | $9.086 \cdot 10^{-6}$ | 2.113 | 5.620 | 0.6498 | $6.748 \cdot 10^{-15}$ |
| 2 | 7.5 | 4.27 | −1.037 | 0.0864 | $6.555 \cdot 10^{-6}$ | 2.527 | 4.906 | 0.6273 | $1.898 \cdot 10^{-14}$ |
| 3 | 15 | 4.06 | −1.022 | 0.0921 | $5.937 \cdot 10^{-6}$ | — | 4.850 | 0.5884 | $1.249 \cdot 10^{-14}$ |
| 4 | 30 | 3.79 | −0.980 | 0.0919 | $5.157 \cdot 10^{-6}$ | — | 4.895 | 0.5895 | $2.885 \cdot 10^{-13}$ |
| 5 | 45 | 3.24 | −0.975 | 0.0866 | $3.765 \cdot 10^{-6}$ | 2.885 | 4.590 | 0.6259 | — |
| 6 | 60 | 2.89 | −0.964 | 0.0885 | $3.007 \cdot 10^{-6}$ | 3.562 | 4.634 | 0.6124 | $1.340 \cdot 10^{-13}$ |
| | | | | | Co(II) | | | | |
| 1 | 0 | 6.96 | −1.305 | 0.0956 | $1.737 \cdot 10^{-5}$ | 1.105 | 7.776 | 0.5665 | $9.770 \cdot 10^{-16}$ |
| 2 | 7.5 | 5.07 | −1.296 | 0.1077 | $9.217 \cdot 10^{-6}$ | 1.797 | 5.820 | 0.5003 | $2.468 \cdot 10^{-14}$ |
| 3 | 15 | 4.62 | −1.280 | 0.1222 | $7.652 \cdot 10^{-6}$ | 1.989 | 5.707 | 0.4435 | $6.981 \cdot 10^{-13}$ |
| 4 | 30 | 4.13 | −1.270 | 0.1356 | $6.141 \cdot 10^{-6}$ | 2.129 | 5.335 | 0.3997 | $6.488 \cdot 10^{-12}$ |
| 5 | 45 | 3.59 | −1.245 | 0.1500 | $4.643 \cdot 10^{-6}$ | 2.340 | 5.093 | 0.3613 | $5.351 \cdot 10^{-11}$ |
| 6 | 60 | 2.80 | −1.227 | 0.1610 | $2.822 \cdot 10^{-6}$ | 3.016 | 4.489 | 0.3366 | $1.751 \cdot 10^{-10}$ |
| | | | | | Mn(II) | | | | |
| 1 | 0 | 6.96 | −1.465 | 0.0325 | $1.737 \cdot 10^{-5}$ | 1.105 | 7.776 | | |
| 2 | 7.5 | 5.37 | −1.484 | 0.0344 | $1.020 \cdot 10^{-5}$ | 1.624 | 6.186 | | |
| 3 | 15 | 5.07 | −1.492 | 0.0386 | $9.217 \cdot 10^{-6}$ | 1.651 | 6.046 | | |
| 4 | 30 | 4.62 | −1.508 | 0.0360 | $7.652 \cdot 10^{-6}$ | 1.709 | 5.964 | | |
| 5 | 45 | 4.13 | −1.519 | 0.0360 | $6.430 \cdot 10^{-6}$ | — | — | | |
| 6 | 60 | 3.72 | −1.544 | 0.0360 | $4.962 \cdot 10^{-6}$ | 1.838 | 5.975 | | |

of "$i_{d\eta^{1/2}}$" conclusively suggest the change in the size of the ion i.e. solvation. Limiting current have simple relation to viscosity but deviation occur due to varying degrees of solvation of the ion[4]).

The dipolar character may give rise to clusters around the electroreducible ion. The dipolarizer ions may be attached to the solvent molecules by chemical forces or physical forces or both and hence the effective radius may not remain constant.

Since the diffusion coefficient is related to the mobility of the diffusing molecule or ion by

$$D = \frac{RT}{K}\, \delta$$

where

$$= \text{mobility} = \frac{1}{6\pi\eta r}$$

combining the two

$$D = \frac{RT}{K} \cdot \frac{1}{6\pi\eta r}$$

assuming the medium to be continuous w.r.t. the diffusing molecule so that the retrading forces are entirely frictional in nature and proportional to viscosity of the solution, "r" is evaluated by

$$r = \frac{RT}{K}\,\frac{1}{6\pi\eta D} \quad \text{where } R = 8.315 \cdot 10^7 \text{ ergs deg}^{-1}$$

$$T = 298\,^\circ K \ (25\,^\circ C)$$

$$K = 6.03 \cdot 10^{23}$$

$$r = \frac{21.79 \cdot 10^{-16}}{\eta D} \text{ at } 25\,^\circ C.$$

The values of "r" vary in each case and this increases with the increasing content of formamide. The inconstancy in "$i_{d\eta^{1/2}}$", change in ionic radius "r" and D as a result of the variation in the size of the ion are the factors which safely lead to the conclusion that the solvation plays a dominant role. This in turn affects all the values of $i_d$.

The changes in $E_{1/2}$ may be due to the solvent molecules entering into the primary solvation sheath of the cations and the changes in the contribution to the half-wave potential of the ion dipole interaction. In the presence of higher concentration of organic substance, association of the metal ion with anions in the solution may also take place (ion-pair formation). The other plausible factors responsible for the variation of $E_{1/2}$ may be 1. change resulting from any alteration in $H^+$ activity of the aqueous solution. 2. any change in the potential of d.m.e. or change due to the introduction of a liquid junction potential, though it is neglibily small and 3. any effect on the inherent reduction potential of the reducible compound.

Since Zn(II), Ni(II) and Co(II) exhibit irreversible character, a brief discussion in connection with their rate constants is as follows.

### Zinc as depolarizer

Zinc yields a well defined and diffusion controlled wave in presence of 1 M NaClO$_4$ with $E_{1/2} = -1.013$ volts vs S.C.E. with increasing percentage of formamide the $E_{1/2}$ is slightly shifted to more negative side the reasons

for which have already been pointed out. Slope determinations from plots of E vs (log $i/i_d$ — i) and ($E_{3/4}$ — $E_{1/4}$) show that the reduction is highly irreversible. The calculations of factors $\alpha_{na}$ and "$K_{f,h^o}$" show that the both increase with the increase of formamide contents. The increase in "$K_{f,h^o}$" shows the tendency of the wave towards reversibility although values lower than $3 \cdot 10^{-5}$ cm/sec. bears testimony to an irreversible process.

## Nickel and Cobalt depolarizers

Ni(II) and Co(II) in presence of 1 M $NaClO_4$ give well defined waves with $E_{1/2}$ being — 1.050 and — 1.305 volts vs S.C.E. respectively. In presence of formamide the $E_{1/2}$ is shifted to more positive potential with the increase in the percentage of formamide. This is in concurrence with the observation KOLTHOFF[8][9]). Slope determinations in the cases also indicate that the reduction is irreversible.

## Mangenese as depolarizer

As already indicated slope determinations in this case indicate that the reduction is reversible and therefore, MEITES and ISRAEL equation is not applicable and factors "$\alpha_{na}$" and "$K_{f,h^o}$" have not be calculated.

[8]) I. M. KOLTHOFF and J. J. LINGANE, "Polarography Vol. I" Inter Science Pub. p. 97 (1955).

[9]) I. ZLOTOWSKI and I. M. KOLTHOFF, J. Amer. chem. Soc. 64, 1297 (1942).

Agra (India), Department of Chemistry, Agra College.