

- (i) 2 ml Sup. soln + 38 ml water/methanol
- (ii) 4 ml Sup. soln + 36 ml water/methanol
- (iii) 38 ml Sup. soln + 2 ml water/methanol
- (iv) 40 ml Sup. soln + 0 ml water/methanol

In the supernatant liquid, lithium was estimated as lithium periodate, Li_5IO_6 , complex ion². The results of lithium determination were also verified flame photometrically using Carl Zeiss flame-photometer with Li67J filter. At least two separate determinations were carried out for each estimation. Cuprous ions were estimated volumetrically.

The concentration of wet residue in equilibrium with the mother liquor was obtained by subtracting the concentrations of CuX and LiX (as determined from the analysis) from the initial concentrations of CuX and LiX in the absence of any precipitation.

The complex ion formation in the solid phase was determined by rectangular and triangular phase diagrams, while in the liquid phase, both conductometric and potentiometric techniques were used for the aqueous solutions and only conductometric technique was used for the studies in methanolic medium. Similarly only rectangular diagrams have been used for methanolic medium.

The conductometric and potentiometric studies were made using the same stock solutions (as taken during analytical studies) and all the observations were made with mixture kept in a thermostat at $30 \pm 1^\circ\text{C}$. The cuprous halides and water or methyl alcohol were mixed in the same order as done for the analytical studies. The conductometric studies were carried out using a W. G. Pye resistance box. A portable Pye potentiometer Cab. No. 7569 P with the lamp and scale arrangement was used for determining the potentials.

The results summarised in Table 1 show presence of complex compounds corresponding to complex ions ranging from CuX_2^- to CuX_4^{3-} and addition compounds. The complexes LiCuCl_2 , Li_2CuCl_3 , Li_3CuBr_4 , LiCuI_2 , LiCuI_3 , Li_2CuI_3 and Li_3CuI_4 exist in solid phase. In the liquid phase, while

Li_3CuCl_4 and Li_4CuI_4 can logically be characterised as complexes, Li_4CuCl_5 or CuCl_4LiCl , Li_4CuI_5 or CuI_4LiI and CuBr_5LiBr may be considered as addition compounds.

In the methanolic system, the mode of complex formation in the solid phase is, more or less, the same as in the aqueous medium.

It is noteworthy that inspite of the comparatively greater solubility of Cu(I) halides in the respective lithium halides in methanolic medium, there is not a single complex in which more than three halide ions are bound to the central Cu(I) atom. This tendency is exhibited by complexes both in the solid and the liquid phases. Furthermore, there is addition compound formation in the liquid phase which is not observed in the aqueous medium. Cuprous halides in the aqueous medium dissolve only when there is high halide concentration, otherwise they get hydrolysed, a process which is not expected in methanol. At higher halide concentrations in aqueous medium, it is expected that more and more halide atoms would be available for bonding to the central Cu(I) atom. Moreover, methanol itself binds with the Cu(I) restricting the bonding of halide ions.

References

- PETERS, D. G. & CALDWELL, R. L., *Inorg. Chem.*, **6** (1967), 1478.
- REGERS, L. B. & CLAY, E. R., *Ind. Eng. Chem. Anal. Ed.*, **15** (1943), 209.

Effect of Dicyandiamide & Related Organic Compounds on Anodic Dissolution of Nickel in Sulphuric Acid

AMARNATH MAITRA*†, KALYAN BHATTACHARYYA & GURMEET SINGH‡

Department of Chemistry, University of Delhi, Delhi 110 007

Received 14 October 1980; revised and accepted 29 May 1981

Anodic dissolution of nickel in sulphuric acid has been studied in the presence of dicyandiamide, biguanide and guanylurea. The effects of these organic additives on the passivation parameters like primary passivation potential, critical current density and passive current density are governed by the adsorbabilities of the additives on the metal surface at different anodic potentials in acid solutions, and the abilities of the additives to form complexes with the surface metal oxides and hydroxides. Synergistic effects of these organic compounds in the presence of traces of halide ions have also been studied and it has been shown that the interactions of these organic compounds with the metal surface are governed mainly by the already adsorbed halide ions at the interface and their specific adsorbabilities.

THE anodic dissolution of nickel in different acid solutions in the presence of different organic and inorganic additives has received recent attention¹. We have recently used dicyandiamide, guanylurea

TABLE 1 — COMPOSITIONS OF COMPLEXES AND ADDITION COMPOUNDS OF VARIOUS SYSTEMS IN AQUEOUS AND METHANOLIC MEDIA DETERMINED BY PHASE DIAGRAMS AND ELECTROMETRIC METHODS

CuCl-LiCl-H ₂ O/ MeOH	CuBr-LiBr-H ₂ O/ MeOH	CuI-LiI-H ₂ O/ MeOH
AQUEOUS SYSTEM		
$\text{LiCuCl}_2^{a, b, s}$	$\text{Li}_3\text{CuBr}_4^{a, b, s}$	$\text{LiCuI}_2^{a, b, s}$ $\text{Li}_2\text{CuI}_3^{a, b, s}$ $\text{Li}_3\text{CuI}_4^{a, b, c, d}$ $\text{Li}_4\text{CuI}_5^c$ or $\text{CuI} \cdot 4\text{LiI}$
$\text{Li}_2\text{CuCl}_3^{a, s}$	$\text{CuBr} \cdot 5\text{LiBr}^c, d$	
$\text{Li}_4\text{CuCl}_5^c$ or $\text{CuCl} \cdot 4\text{LiCl}$		
METHANOLIC SYSTEM		
LiCuCl_2^a $\text{Li}_2\text{CuCl}_3^c$	$\text{Li}_2\text{CuBr}_3^a$ $\text{Li}_2\text{CuBr}_3^c$	LiCuI_2^a, c

a, rectangular diagram; b, triangular diagram; c, conductometric method; d, potentiometric method; s, solid phase; l, liquid phase.

*Present address: Physikalisch-Chemisches Institut der Universität Basel, 4056 Basel, Switzerland.

‡Present address: S. G. T. B. Khalsa College, Delhi University, Delhi 7.

and biguanide as potential corrosion inhibitors² and in this note we report the inhibition action of these compounds during anodic dissolution of nickel in acid solution.

Nickel beads (Johnson Mathey, 99.99%) were used as such. The detailed procedure for surface preparation of the beads and the synthesis of the organic additives have been reported elsewhere^{2d}. The electrode was polarised potentiostatically. Potential increments of 20mV were applied very slowly for 5 min and once the potential was set the corresponding current reading was noted after 5 min. Since the shape of the potentiostatic curves is affected by a large number of factors such as rate of change of potential, surface preparation, etc. these parameters were kept uniform throughout the experiment as far as practicable. All connections to the potentiostat were of shielded type. Potentials were recorded against saturated calomel electrode. All the potentiostatic studies were carried out in air saturated solutions at $25 \pm 1^\circ\text{C}$ in 1N H_2SO_4 .

The dissolution parameters like primary passivation potential (E_{pp}), critical current density (I_c) and passive current density (I_p) of nickel in sulphuric acid with and without additives are shown in Tables 1 and 2. Additions of organic compounds do not shift the E_{pp} of nickel significantly except in the case of biguanide which causes considerable shift in E_{pp} towards the nobler direction. Negligible changes in the critical current densities, I_c , were observed for nickel in sulphuric acid containing dicyandiamide and guanylurea while increase in [biguanide] caused an increase in I_c . The presence of halide ions caused considerable change in the dissolution parameters of nickel. E_{pp} of nickel shifted from +80mV in pure acid to +165mV in solution containing iodide ions. A significant decrease in I_c was also observed in presence of iodide ions. Chloride ions did not change E_{pp} but increased the critical current densities, I_c . Effect of bromide ions was intermediate. Change of dissolution parameters was found to be maximum in biguanide-iodide system.

The dissolution parameters of nickel during steady-state potentiostatic polarisation in sulphuric acid

TABLE 1 — PASSIVATION PARAMETERS OF ACID DISSOLUTION OF NICKEL IN THE PRESENCE OF ORGANIC ADDITIVES IN 1N SULPHURIC ACID

Additive	E_{pp} (vs SCE) (mV)	I_c (mA/cm ²)	I_p (mA/cm ²)
Nil	+85	9.9	2.5×10^{-2}
$10^{-5}M$ Dicyandiamide	+80	10.0	2.2×10^{-2}
$10^{-3}M$ „	+82	8.6	4.0×10^{-2}
$10^{-1}M$ „	+80	12.0	2.0×10^{-2}
$10^{-5}M$ Biguanide	+80	19.5	2.7×10^{-1}
$10^{-3}M$ „	+90	25.0	2.7×10^{-1}
$10^{-1}M$ „	+125	55.0	4.4×10^{-2}
$10^{-5}M$ Guanylurea	+85	16.0	7.5×10^{-1}
$10^{-3}M$ „	+75	12.0	3.0×10^{-2}
$10^{-1}M$ „	+75	8.8	2.2×10^{-2}

TABLE 2 — PASSIVATION PARAMETERS OF ACID DISSOLUTION OF NICKEL IN THE PRESENCE OF ORGANIC ADDITIVES IN 1N SULPHURIC ACID CONTAINING HALIDE IONS

Additive	E_{pp} (vs SCE) (mV)	I_c (mA/cm ²)	I_p (mA/cm ²)
Nil	+85	9.9	2.5×10^{-2}
$10^{-4}M$ KCl	+82	36.0	9.0×10^{-2}
$10^{-4}M$ KBr	+82	15.0	3.0×10^{-2}
$10^{-4}M$ KI	+165	1.9	3.4×10^{-1}
$10^{-4}M$ KCl+ $10^{-3}M$ Dm	+85	22.0	3.2×10^{-2}
$10^{-4}M$ KCl+ $10^{-3}M$ Big	+88	13.0	2.5×10^{-2}
$10^{-4}M$ KCl+ $10^{-3}M$ GU	+82	21.0	2.0×10^{-2}
$10^{-4}M$ KBr+ $10^{-3}M$ Dm	+80	15.0	2.1×10^{-1}
$10^{-4}M$ KBr+ $10^{-3}M$ Big	+82	7.8	2.5×10^{-1}
$10^{-4}M$ KBr+ $10^{-3}M$ GU	+82	23.5	3.2×10^{-1}
$10^{-4}M$ KI+ $10^{-3}M$ Dm	+162	1.15	1.4×10^{-2}
$10^{-4}M$ KI+ $10^{-3}M$ Big	+165	2.35	2.4×10^{-2}
$10^{-4}M$ KI+ $10^{-3}M$ GU	+165	9.8×10^{-1}	1.8×10^{-2}

Dm—Dicyandiamide; Big—Biguanide; GU—Guanylurea.

(Table 1) are in good agreement with those reported by others³. In the trans-passive region, the current increases rapidly with the increase in potential and the tafel behaviour is clearly observed for trans-passive dissolution of nickel in sulphuric acid. Tafel slope is found to be 150mV/decade which is in good agreement with the values reported earlier⁴.

The interaction of these organic compounds with the surface metal atoms, metal oxides and hydroxides and the consequent influence of these compounds on the various dissolution parameters may be interpreted in terms of the electronic structures of the organic additives. Dicyandiamide, guanylurea and biguanide are conjugated molecules having extensively delocalised π -electron systems and the π -orbitals cover all the molecular atoms. Each molecule is having guanyl part which is basic and in acid solution it has a tendency to remain protonated. Moreover, biguanide and guanylurea form chelates with transitional metal ions⁵. In the open-circuit potential the compounds are expected to be adsorbed on the metal surface through the d_{π} - p_{π} interactions.

In the active potential range, biguanide increases the critical current density of nickel. The catalytic activity of biguanide seems to be due to the interaction of the adsorbed surface hydroxyl groups with the protonated biguanide which causes greater exposure of the metal surface to the corrosive media. Relatively less basic guanylurea and significantly less basic dicyandiamide do not interact in this way at the interface and are desorbed in the active potential range. Nickel surface in the presence of dicyandiamide and guanylurea behaves in the same way as that in pure sulphuric acid. Biguanide increases the passive current density (I_p) and shifts the primary passivation potential (E_{pp}) towards the nobler direction. In the passive potential range the influence of these additives is expected to be

governed by two opposing effects, viz. (i) adsorption of the inhibitor on the metal surface which prevents oxide layer formation (I_p increases) and (ii) formation of the insoluble metal hydroxide-inhibitor complexes on the electrode surface which act as physical barriers to metal dissolution reaction (I_p decreases). The second effect predominates at higher inhibitor concentration and for a stronger complexing agent like biguanide whereas the first effect acts primarily at lower inhibitor concentration and for weaker complexing agents. Studies on the anodic dissolution of iron in the presence of some inhibitors have indicated that in the passive region the adsorbed inhibitors (In) participate in the reaction in the form of complex of the type $(\text{Fe-In})_{\text{ads}}$ or $(\text{Fe-OH-In})_{\text{ads}}$ and the dissolution reaction proceeds less readily via adsorbed inhibitor complexes than via $(\text{Fe-OH})_{\text{ads}}$ and hence the passive current is decreased⁶. Sometimes both the rates are comparable and the metal dissolution reaction follows an intermediate path. In the present case perhaps biguanide and guanylurea form the adsorbed species of the former type and thus the blanketing effect of $(\text{Ni-In})_{\text{ads}}$ or $(\text{Ni-OH-In})_{\text{ads}}$ complex is comparable to the rate of dissolution of these adsorbed complexes in the acid medium as follows :



Feller *et al.* and others^{1e} have studied the effect of halide ions on the anodic passivation of nickel. They have observed that even a small addition of halide ions to 1*N* sulphuric acid results in marked deviation in current density-potential curves from those obtained in pure sulphuric acid. These changes, appearing in the potential range between hydrogen evolution and onset of passivity, are explained on the basis of the varying contact adsorption of the different halide ions. Adsorption of organic cations and onium compounds, which exist in the cationic form in the acid solution, increases sharply on addition of halide ions in sulphuric acid solutions⁷. Moreover these types of organic cationic species are weakly adsorbed on the nickel surface at the open circuit potential because the pzc of nickel in sulphuric acid is nearly zero⁷.

As shown in Table 2, iodide ions shift the primary passivation potential towards the nobler direction, decrease the critical current density considerably and increase the passive current; whereas chloride and bromide ions have insignificant influence on the primary passivation potential and passive current density but the critical current densities are increased considerably. The increase in the critical current densities due to the presence of chloride ions is suppressed in the presence of all the additives. This suppression is found to be maximum in the presence of biguanide. A considerable variation in critical current densities has been found in the case of solution containing guanylurea with bromide ions. Only a small variation of this parameter has been found in the case of biguanide. In the active region there are three types of species to be adsorbed on the metal surface, viz. the organic additive

(molecule/cation), halide ions and SO_4^{2-} or HSO_4^- ions. The competitive adsorption of these species depends on the specific adsorbabilities of the organic species and other ions and the charge of the metal surface at the active potential region. Mikhailova and Iofa^{1m} have studied the adsorption and inhibition action of organic cations on nickel surface and found that the adsorbabilities of the organic species increase in presence of halide ions in the sequence : $\text{Cl}^- < \text{Br}^- < \text{I}^-$. This is due to the more stable chemisorption of iodide ions because of easy deformability of their electron shells. In presence of all these organic additives, the primary passivation potentials remain almost the same as those in halide containing solutions. The suppression of critical current densities by the organic additives was observed in presence of Br^- and Cl^- ions which was thought to be due to ion-pair or dipolar interactions between the adsorbed halide ions and organic cations or molecules.

Financial support from the CSIR, New Delhi, is thankfully acknowledged by the authors.

References

- 1(a) WENDT, W. & FELLER, H. F., *Metalik*, **Z.** **61** (1970), 718. (b) FELLER, H. G. & RATZER-SCHIEBE, H. G., *Elektrochim. Acta*, **17** (1972), 178. (c) FELLER, H. G., KESTEN, M. & KRUPSKI, J., *Proc. 5th Cong. Met. Corros.*, 1972, Publ. 1974, pp 155-159. (d) PETIT, M. C. & JOUANNEAU, A., *Proc. 5th Int. Cong. Met. Corros.* 1972, Publ. 1974, pp 237. (e) FELLER, H. G., RATZER-SCHIEBE, H. G. & WENDT, W., *Electrochim. Acta*, **18** (1973), 175. (f) GRAZ, I. & GLAZER, B., *Corros. Sci.* **14** (1974), 353. (g) BARKALATSOVA, L. A. & PSHENICKNIKOV, A. G., *Elektrokhimiya*, **12** (1976), 42. (h) BALASHOVA, N. A., GOROKOVA, N. T., KULENZNOVA, N. I. & LIBIN, S. A., *Chem. Abstr.*, **84** (1976), 186580b. (i) KESTEN, M., *Corrosion*, **32** (1976), 94. (j) KESTEN, M. & SUSSEK, G., *Werk. u. Korros.*, **27** (1976), 77. (k) SORUKHIM, I. L., TEDORADZE, G. A., KAUROVA, G. I. & RAZMEROVA, T. I., *Elektrokhimiya*, **12** (1976), 442. (l) MIKHAILOVA, E. I. & IOFA, Z. A., *Elektrokhimiya*, **12** (1976), 664. (m) BREUSHKE, H., WELLER, F. & EBERT, K. H., *Werk. u. Korros.*, **27** (1976), 227. (n) MAITRA, A. N., HECHT, A., DROSTE, B. & FELLER, H. G., *Metalloberfläche*, **33** (1979), 112.
- 2(a) MAITRA, A. N. & CHAKRAVORTY, B. B., *Corros. Sci.*, **14** (1974), 511. (b) MAITRA, A. N. & BARUA, S., *Corros. Sci.* **14** (1974), 587. (c) MAITRA, A. N. & SINGH, G., *Indian J. Chem.*, **18A** (1980), 111. (d) MAITRA, A. N. & BHATTACHARYYA, K., *Trans. SAEST*, **14** (1979), 221. (e) MAITRA, A. N., BHATTACHARYYA, K. & SINGH, G., *Trans. SAEST*, (in press), (f) MAITRA, A. N. SINGH, G. & CHAKRAVORTY, B. B., *Brit. Corros. J.* (in press).
- 3(a) VETTER, K. & ARNOLD, K., *Z. Elektrochem.*, **64** (1960), 244, 407. (b) OKAMOTO, G., KOBAYASHI, H., NAGAYAMA, M. & SATO, N., *Z. Elektrochem.*, **62** (1958), 775. (c) KOLOTYRKIN, Y., *Z. Elektrochem.*, **62** (1958), 664. (d) SAYANO, R. R. & KEN, NOBE, *Corrosion*, **22** (1966), 81.
4. OSTERWALD, J., & UHLIG, H. H., *J. Electrochem., Soc.*, **108** (1961), 515. (b) KUNZE, B. & SCHWABE, K., *Corros. Sci.*, **4** (1964), 109.
5. RAY, P., *Chem. Rev.*, **61** (1961), 315.
6. *Corrosion*, Vol. II, Edited by L.L. Shreir (Newnes Butterworths, London), 1976, 18; 36.
7. DAMASKIN, B. B., PETRII, A. & BATRAKOV, V. V., *Adsorption of organic compounds* (Plenum Press, London), 1971, 262.