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Borate buffer equilibria in nickel refining electrolytes

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Buffer capacity studies, carried out using pH titrations, demonstrated that electrolytes containing $NiSO_4 + H_3BO_3 + Na_2SO_4$ buffer more effectively than in the presence of $H_3BO_3 + Na_2SO_4$. The increased buffer capacity is dependent on the concentration of both Ni^{2+} and H_3BO_3. Thermodynamic analysis of the pH titration data suggested the formation of a weak complex, $Ni(H_2BO_3)_2$, ($\log K \sim 3{\cdot}8$ to $4{\cdot}9$) between Ni^{2+} and H_3BO_3 in mixed chloride-sulphate electrolytes at 55° C.

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1. Introduction

Nickel is conventionally electrodeposited from sulphate or sulphate-chloride electrolytes containing boric acid in the pH region of 3–5. This pH range is preferred because, during electrodeposition of nickel, H^+ is simultaneously discharged with Ni^{2+}, resulting in a low current efficiency for nickel deposition in acid solutions and precipitation of $Ni(OH)_2$ at high pH values. The latter is undesirable since it affects the quality and nature of the electrodeposits. Even in the pH range of 3–5, $Ni(OH)_2$ formation would occur if the solution was not sufficiently agitated or buffered (since the pH at the cathode interface would be > 5) and hence, boric acid additions become mandatory.

It is generally stated in the literature that boric acid buffers nickel electrolytes in the pH region of ~ 5, based on pH-titration curves. However, the reactions governing the equilibria responsible for regulating the pH in Ni electrolytes have not been elucidated. An attempt was therefore made to understand the buffer characteristics of electrolytes containing $NiSO_4$ + boric acid. In the present study, a typical electrolyte used in nickel refineries, containing 60 $g\,l^{-1}$ Ni, 78 $g\,l^{-1}$ NaCl, 47 $g\,l^{-1}$ Na_2SO_4, and 19 $g\,l^{-1}$ H_3BO_3 was chosen.

2. Experimental

pH titrations were carried out with the following solutions prepared from Analar grade reagents, at $55 \pm 0{\cdot}5$° C.

(1) 0·97 M $NiSO_4$ (+ 1·33 M NaCl + 0·33 M Na_2SO_4) and boric acid concentrations ranging from 0·1 to 0·5 M.

(2) 0·3 M H_3BO_3 (+ 1·33 M NaCl + 0·33 M Na_2SO_4) and $NiSO_4$ concentrations ranging from 0·1 to 0·5 M.

The following procedure was adopted during the pH titrations. 100 ml of solution at a pH of ~ 3 was titrated with 2 N NaOH added in 0·02 ml aliquots until a pH of 5·5 was reached. The solution was well stirred and the pH of the clear solution was measured with a glass electrode using a Corning scientific instrument model 7 pH meter.

3. Results

pH titration curves obtained with the above electrolytes are shown in Figs. 1 and 2. Buffer capacity values (expressed in g equiv. of alkali required to raise the pH of 1 litre of solution from a value of 4–5·5) were calculated from the pH titration curves. The dependence of buffer capacity on H_3BO_3 concentration (at constant Ni ion concentration) and on Ni ion concentration (at constant boric acid concentration) is shown in Figs. 3 and 4. It is seen that the buffer capacity increases in both cases as either the nickel ion or boric acid concentration is increased in the pH region of 4–5·5.

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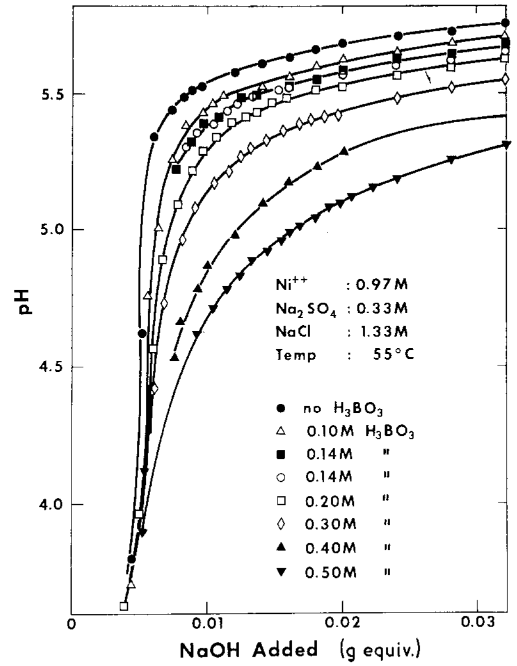

Fig. 1. Variation of pH with the amount of NaOH (in g equiv.) added l^{-1} of the electrolyte containing 0·97 M Ni^{2+} + 0·33 M Na_2SO_4 + 1·33 M NaCl and varying amounts of boric acid.

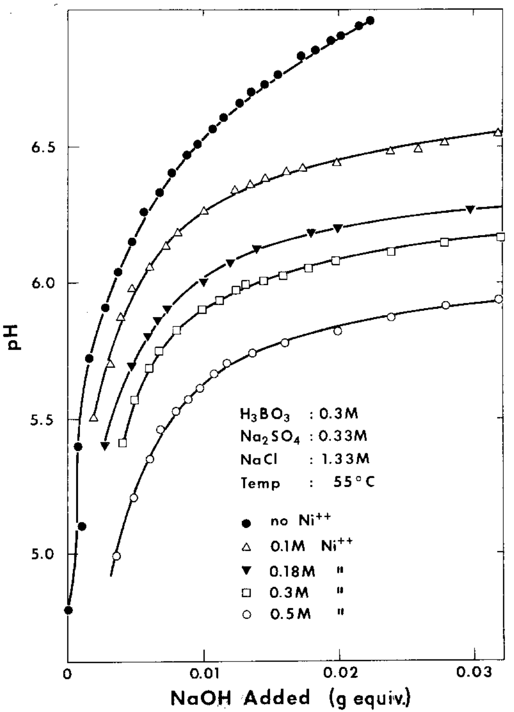

Fig. 2. Variation of pH with the amount of NaOH (in g equiv.) added l^{-1} of the electrolyte containing 0·3 M H_3BO_3 + 0·33 M Na_2SO_4 + 1·33 M NaCl and varying concentration of Ni^{2+} ion.

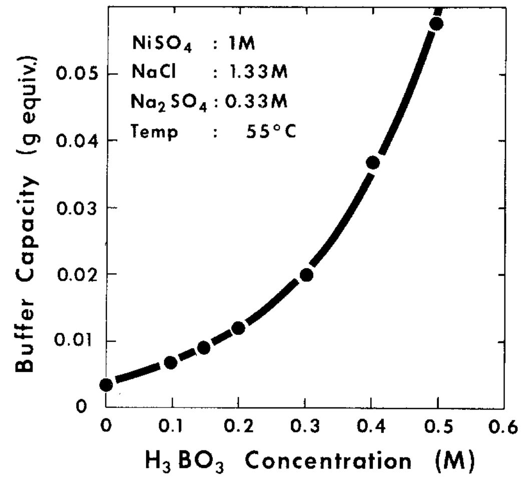

Fig. 3. Variation of buffer capacity (in g equiv. l^{-1}) with boric acid concentration (in mol l^{-1}) of the electrolyte containing 1 M $NiSO_4$ + 1·33 M NaCl + 0·3 M Na_2SO_4 at 55° C.

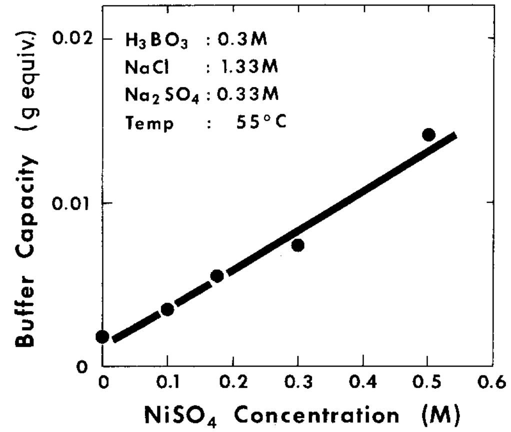

Fig. 4. Variation of buffer capacity (in g equiv. l^{-1}) with $NiSO_4$ concentration (in mol l^{-1}) of the electrolyte containing 0·3 M H_3BO_3 + 1·33 M NaCl + 0·3 M Na_2SO_4 at 55° C.

4. Discussion

The increase in buffer capacity of $NiSO_4$ + H_3BO_3 electrolytes compared to that of either pure $NiSO_4$ or pure H_3BO_3 solutions, and the decrease in pH noticed when $NiSO_4$ solutions and H_3BO_3 at the same pH are mixed, suggests a specific interaction between Ni^{2+} ions and H_3BO_3 in aqueous solutions and rules out the possibility of boric acid dissociation equilibria alone as contributing towards the buffer action observed in boric acid-containing Ni electrolytes. Complex formation namely $Ni(OH)_2$–

$2H_3BO_3$, based on optical studies of $NiSO_4$ + H_3BO_3 solutions at different pH values, has been invoked [1] to explain the above deviation from the law of isohydric solutions. Such a mechanism however, is unlikely to be operative below the pH for the precipitation of $Ni(OH)_2$.

In order to explain the effects of boric acid and Ni^{2+} ion concentration on the pH titration curves, a thermodynamic method has been used, wherein the ionic concentrations of all the relevant species in the solution were taken into consideration. In addition, a 'buffer capacity method' [7] which involves the prediction of gross changes in pH based on an assumed reaction sequence has also been employed to analyse the data.

4.1. *Thermodynamic analysis*

The significant reactions involving Ni^{2+} and H_3BO_3 may be described as follows:

$$H_3BO_3 \overset{k_1}{\rightleftharpoons} H^+ + H_2BO_3^- \qquad (1)$$

$$Ni^{2+} + 2H_2BO_3^- \overset{k_2}{\rightleftharpoons} Ni(H_2BO_3)_2 \qquad (2)$$

(denoted as NiB_2)

$$Ni^{2+} + SO_4^{2-} \overset{k_4}{\rightleftharpoons} NiSO_4 \qquad (3)$$

$$Ni^{2+} + H_2O \overset{k_5}{\rightleftharpoons} NiOH^+ + H^+. \qquad (4)$$

The appropriate mass balance and electroneutrality relationships assuming the presence of the above species are:

$$T_{Ni} = Ni^{2+} + NiB_2 + NiOH^+ + NiSO_4 \qquad (5)$$

$$T_B = H_3BO_3 + H_2BO_3^- + 2NiB_2 \qquad (6)$$

$$T_{SO_4} = SO_4^{2-} + NiSO_4 \qquad (7)$$

$$2Ni^{2+} + H^+ + Na^+ + NiOH^+ = 2SO_4^{2-} + OH^- + H_2BO_3^-. \qquad (8)$$

According to the above formulation, the buffer action arises from the dissociation of H_3BO_3 to H^+ ions (which neutralize the OH^- ions) and $H_2BO_3^-$ ions which complex the Ni^{2+} species to form NiB_2. The amount of alkali consumed depends on the amount of NiB_2 formed and hence an estimate of the stability constant k_2 would indicate the relative strength of the complex formed via the interaction of Ni^{2+} and $H_2BO_3^-$ ions.

In order to calculate the equilibrium constant, k_2, for the complex formation, it is necessary to express the free or unbound H_3BO_3, Ni^{2+}, and SO_4^{2-} concentrations in terms of the total concentrations (T). Thus, from Equations 5, 6 and 8, the concentration of free H_3BO_3 and $H_2BO_3^-$ may be expressed as follows:

$$(H_3BO_3) = \alpha + A(Ni) \qquad (9)$$

$$(H_2BO_3^-) = X + B(Ni) \qquad (10)$$

where

$$\alpha = OH^- - H^+ - Na^+ + 2T_{SO_4} - 2T_{Ni} + T_B$$

$$X = \frac{k_1\alpha}{H};\ A = \frac{k_5(H_2O)}{H^+};\ B = \frac{k_1 A}{H^+}.$$

The free Ni ion concentration (Ni) can be calculated from Equations 6 and 8–10 from the quadratic equation,

$$(Ni)^2 D + (Ni)E - \delta = 0 \qquad (11)$$

where

$$D = k_4(2 + C - \delta);\ E = 2 + C + 2k_4 T_{SO_4};$$

$$\delta = 2T_{Ni} - q;\ q = T_B - \alpha - X;\ C = A - B.$$

(D, δ, E, q and C are experimentally accessible quantities.) Substitution of (Ni) into Equation 6 leads to a simple relationship

$$y = k_2 z \qquad (12)$$

where

$$y = q - (Ni)(A + B)$$

$$z = 2((Ni)X^2 + 2(Ni)^2 XB + (Ni)^3 B^2).$$

Thus, a plot of y versus z should result in a straight line of slope k_2, and intercept at the origin.

The values of k_4, k_5 and k_w required for the above calculation were taken from the literature and are as follows:

$k_4 = 3{\cdot}7$ (at 25° C and ionic strength 1·0 [2]);

$k_5 = 10^{-9{\cdot}3}$ (at 50° C in 1 M $NaClO_4$ [3]);

$k_w = 7{\cdot}29 \times 10^{-14}$ (at 55° C [4, 5]).

The value of k_1 deduced from the pH titration data obtained in the presence of H_3BO_3 alone using the expression

$$k_1 = \frac{(H^+)(Na^+ + H^+ - k_w/H^+)}{T_B - Na^+ - H^+ + k_w/H^+} \qquad (13)$$

was found to $10^{-8 \cdot 0}$. This may be compared with the literature values of $-\log k_1 = 8{\cdot}97$ (at 60° C and 0 ionic strength [5]), and 8·59 (at 55° C in 3 M NaCl [6]).

The values of the y–z pairs were computed at each pH value from the pH titration data in Figs. 1 and 2, and plotted in Figs. 5(a) and (b), respectively. These results show reasonable linearity, passing through the origin, in accordance with Equation 12. The minor deviations noticed in Fig. 5(a) can be attributed to the errors in the measured pH values and/or errors in the specific values of T_B, T_{Ni}, T_{SO_4}, etc., as shown by a sensitivity analysis to these parameters. The k_2 value estimated from the slopes was found to be $8{\cdot}1 \times 10^4$ l^2 mol^{-2} from the data in Fig. 5(a) and $6{\cdot}6 \times 10^3$ l^2 mol^{-2} from Fig. 5(b). This discrepancy seems to arise from the differences in the ionic strength of the medium, which is ~ 5·8 for the data shown in Fig. 1 and ~ 3–4 for the electrolyte compositions stated in Fig. 2.

It may be noted that this derived equilibrium constant was not corrected for either the activity coefficients or the ionic strength of the medium. However, this value has significance in the sense that it is valid for the electrolyte composition under study and would provide a reasonable assessment of the relative strength of the complex. The k_2 values deduced above indicate the formation of a weak complex, from which the equilibrium constant for the following overall reaction between Ni^{2+} and H_3BO_3

$$Ni^{2+} + 2H_3BO_3 \xrightleftharpoons{k'} Ni(H_2BO_3)_2 + 2H^+ \tag{14}$$

is estimated in the range of $6{\cdot}6 \times 10^{-13}$ to $8{\cdot}1 \times 10^{-12}$ (or $-\log k' \sim 12{\cdot}2$ to $11{\cdot}1$).

4.2. *'Buffer capacity' analysis*

The thermodynamic approach adopted to calculate the value of the equilibrium constant (K) requires point by point analysis of the pH titration curve. A simpler method was suggested previously [7] which permits determination of K using the buffer capacity values directly, assuming a reaction mechanism for the buffer action. For this purpose, the following equilibrium is postulated for the buffer action of $NiSO_4 + H_3BO_3$ mixtures which involves induced ionization of H_3BO_3 upon complex formation with the Ni^{2+} ion.

$$\begin{gathered} Ni(H_2O)_n^{2+} + xH_3BO_3 \xrightarrow{K} \\ [Ni(H_2O)_{n-x}xH_2BO_3]^{2-x} + xH_3O^+. \end{gathered} \tag{15}$$

On this basis the theory for the buffer action

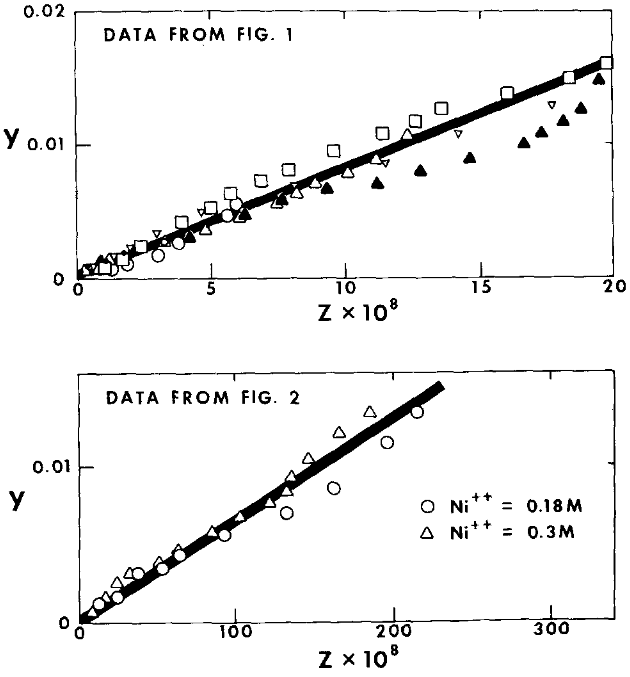

Fig. 5. Plots of y against z using the data in Figs. 1, [5(a)] and 2, [5(b)].

should explain: (a) the additional buffering observed in the presence of H_3BO_3; and (b) the increase in buffer capacity with either H_3BO_3 concentration at constant Ni^{2+} ion concentration or Ni^{2+} ion concentration at constant boric acid concentration. In boric acid-containing electrolytes, a complex is formed releasing H^+ ions and, therefore, extra alkali is required to change the pH from 4–5·5. The amount of alkali needed depends on the extent of complex formation. The concentration of the complex formed is proportional to the quantities of Ni^{2+} and H_3BO_3 and hence buffer capacity should increase with an increase in H_3BO_3 concentration or Ni^{2+} ion concentration.

The number of $H_2BO_3^-$ ligands associated with the Ni^{2+} ion in the complex can now be estimated from the dependence of $\Delta\beta$ (the difference between the buffer capacities of mixtures and pure H_3BO_3) on the H_3BO_3 concentration at constant Ni^{2+} ion concentration.

The quantity of alkali consumed when $NiSO_4$ and H_3BO_3 are mixed, depends on the concentration of the complex and, therefore,

$$\Delta\beta = 0{\cdot}5K\frac{(Ni^{2+})(H_3BO_3)^x}{(H^+)^x(H_2O)^x} \qquad (16)$$

where K refers to the equilibrium constant of Reaction 15. The variation of log $\Delta\beta$ with log (H_3BO_3) (see Fig. 6) was found to be linear according to the theory with a slope of 1·84 ± 0·1. Since x is ≈ 2, the complex can be tentatively considered to be $Ni(H_2O)_{n-2} \cdot 2(H_2BO_3)$. Equation 16 also predicts a proportionality between: (a) log $\Delta\beta$ and log Ni^{2+} at constant H_3BO_3 concentration; and (b) log (H_3BO_3) and pH at constant Ni ion concentration and constant $\Delta\beta$ as demonstrated in Figs. 7 and 8.

An estimate of the formation constant from the intercepts of Figs. 6–8 shows (see Table 1) the value of K to be $\sim 10^{-11}$ which is in fair agreement with the values calculated following the thermodynamic approach.

The formation of a weak neutral complex between Ni^{2+} and H_3BO_3 may also be inferred from: (a) the lack of influence of H_3BO_3 on the Tafel slopes [8]; and (b) the studies [9] on the effect of the double layer structure during the electrodeposition of Ni in Watt's solutions which showed the intermediate species in the electron transfer reaction to be $(NiOH)_{ads}$, with no influence of the species complexed with H_3BO_3.

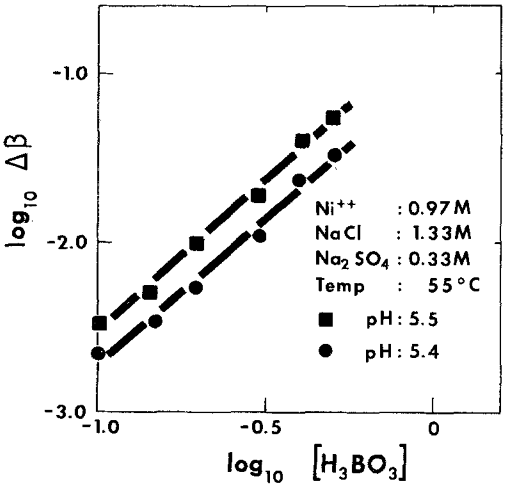

Fig. 6. Variation of $\Delta\beta$ with boric acid concentration, for the conditions stated in the figure, at constant pH.

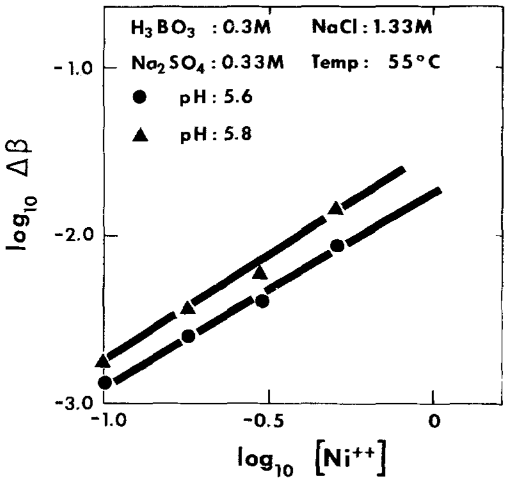

Fig. 7. Variation of $\Delta\beta$ with Ni^{2+} ion concentration, for the conditions stated in the figure, at constant pH.

Thus, the present data are best described in terms of the formation of $Ni(H_2BO_3)_2$ without invoking the monocomplex between Ni^{2+} and $H_2BO_3^-$ ions. The K value deduced is a conditional constant valid only in the concentration range examined in the present study. In view of the high ionic strength of the medium and the difficulty of using the thermodynamic arguments under these conditions, the k_2 values in the range of

Table 1

	Theoretical slope	*Experimental value**	*— log K* (at 55° C)
Log $\Delta\beta$ versus log H_3BO_3 at constant Ni concentration	2·0		
(a) pH = 5·4		1·75 ± 0·1	11·4
(b) pH = 5·5		1·84 ± 0·1	11·4
Log $\Delta\beta$ versus log Ni at constant H_3BO_3 concentration	2·0		
(a) pH = 5·6		1·13 ± 0·1	11·6
(b) pH = 5·8		1·31 ± 0·1	11·7
Log H_3BO_3 versus pH	— 1·0		
Ni = 0·983 M		— 0·87 ± 0·1	9·2
$\Delta\beta = 10^{-3}$ g equiv.			

* These values are based on least square analysis; all the regressions are valid at the 95% confidence level.

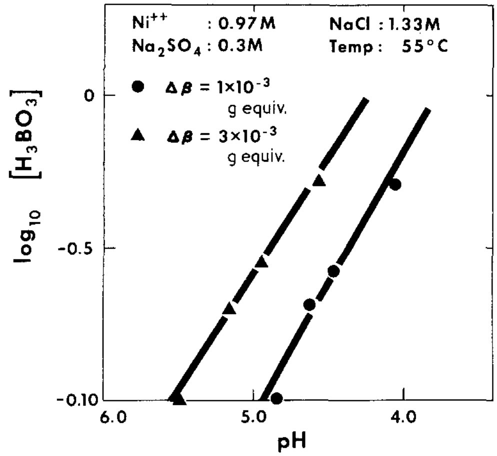

Fig. 8. Variation of log (H_3BO_3) with pH, for the conditions stated in the figure, at constant $\Delta\beta$.

$8{\cdot}1 \times 10^4$ to $6{\cdot}6 \times 10^3$ l^2 mol^{-2} may be considered as satisfactory. Although the formation of a strong complex is not inferred from these values, in the higher pH range (5–6), the effectiveness of the buffering action of $NiSO_4 + H_3BO_3$ solutions would be significant as more $H_2BO_3^-$ would form via the dissociation of H_3BO_3.

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References

[1] A. L. Zhurin and M. G. Shoikhet, *J. Appl. Chem. (U. S. S. R.)* 29 (1958) 641.
[2] N. Tanaka, Y. Saito and H. Ogino, *Bull. Chem. Soc. Japan* 36 (1963) 794.
[3] J. A. Bolzan, E. A. Jauregui and A. J. Arvia, *Electrochim. Acta* 8 (1963) 841.
[4] H. S. Harned and B. B. Owen, 'The Physical Chemistry of Electrolyte Solutions', Reinhold Publishing Corporation, New York (1950).
[5] I. M. Kolthoff and W. Bosch, *Rec. Trav. chim.* 46 (1927) 180.
[6] B. B. Owen and E. J. King, *J. Amer. Chem. Soc.* 65 (1943) 1612.
[7] B. V. K. S. R. A. Tilak, S. R. Rajagopalan and A. K. N. Reddy, *Trans. Faraday Soc.* 58 (1962) 795.
[8] D. M. Chizhikov and L. V. Pliginskaya, *Soviet Electrochemistry* 3 (1961) 69.
[9] I. Epelboin, 21st Meeting of the International Committee on Thermodynamics and Electrochemical Kinetics, Prague (1970).