

UNCERTAINTY INTRODUCED BY EXTRAPOLATION IN THE CONVENTIONAL  
ASSIGNMENT OF REFERENCE pH VALUES

M.J. Guimar H.M. Lito<sup>a)</sup>, M. Filomena G.F.C. Camões<sup>b)</sup>

Centro de Electroquímica e Cinética da Universidade de Lisboa  
R. da Escola Politécnica, 58, 1294 Lisboa Codex

<sup>(a)</sup> Faculdade de Farmácia da Universidade de Lisboa

<sup>(b)</sup> Faculdade de Ciências da Universidade de Lisboa

Conventional assignment of pH standard values, pH(S), is attained from e.m.f. measurement, E, of Harned cells (I) containing the reference buffer solutions under concern to which KCl has been added (keeping the ionic strength, I < 0.1)



Calculated values of the acidity function  $p(a_{\text{H}^+} \gamma_{\text{cl}})$

$$p(a_{\text{H}^+} \gamma_{\text{cl}}) = -\log(a_{\text{H}^+} \gamma_{\text{cl}}) = \frac{E - E^0}{2,3026 RT/F} + \log m_{\text{cl}} \quad (1)$$

are extrapolated to  $m_{\text{cl}} = 0$  in order to overcome the effect of the added chloride.

Addition of KCl introduces minor changes to  $p(a_{\text{H}^+} \gamma_{\text{cl}})$ , particularly in the cases where the buffer concentration exceeds the one of added chloride [1].

For a monoprotic acid, HA, it is



and the acidity function  $p(a_{\text{H}^+} \gamma_{\text{cl}})$  can also be defined in terms of the corresponding acid dissociation constant

$$K = \frac{a_{\text{A}^-} \cdot a_{\text{H}^+}}{a_{\text{HA}}}$$

$$p(a_{H^+} \gamma_{Cl}) = pK + \log \frac{m_A}{\gamma_{HA}} - \log \frac{\gamma_{HA} \cdot \gamma_{Cl}}{\gamma_A} \quad (2)$$

For a buffer ratio  $m_A/m_{HA} = 1$ , the last term being negligible, it is  $p(a_{H^+} \gamma_{Cl}) \approx pK_a$  for all chloride concentrations, independently of ionic strength.

For polyprotic acids, e.g.  $H_3A$  with acid dissociation constants  $K_1$ ,  $K_2$  and  $K_3$ , it is

$$p(a_{H^+} \gamma_{Cl}) = \frac{1}{3} (pK_1 + pK_2 + pK_3) + \frac{1}{3} \log \frac{m_A}{m_{H_3A}} + 2 \log \gamma_1 \quad (3)$$

where  $\gamma_1$  is the activity coefficient of monocharged species.

All other terms being constant, the addition of KCl modifies  $\log \gamma_1$  through the ionic strength, thus introducing a small negative slope for the linear variation of  $p(a_{H^+} \gamma_{Cl})$  vs.  $m_{Cl}$ .

Application of equation (3) to citric acid, 0.01 m  $H_3Cit$ , where



leads to [1]

$$p(a_{H^+} \gamma_{Cl}) = \frac{1}{3} (3.128 + 4.761 + 6.396) + \frac{1}{3} \log 0.047217 \times 10^{-7} - \frac{1}{3} \log 0.0075021 + 2 \log 0.94631 = 2.647$$

Considering all terms constant, except  $\log \gamma_1$  due to the addition of KCl, equation (3) leads to linear representation  $p(a_{H^+} \gamma_{Cl})$  vs.  $m_{Cl}$  of -3.5 slope (Table 1; Fig. 1) and intercept different from 2.647.

TABLE 1. Calculated (equation 3) values of I,  $\log \gamma_1$  and  $p(a_{H^+} \gamma_{Cl})$  for 0.01 m  $H_3Cit$  solutions with added KCl

KCl(m)	I	$\log \gamma_1$	$p(a_{H^+} \gamma_{Cl})$
0	0.0025	-0.023969 [1]	2.647
0.005	0.0075	-0.039151	2.617
0.01	0.0125	-0.048907	2.597
0.015	0.0175	-0.056384	2.582

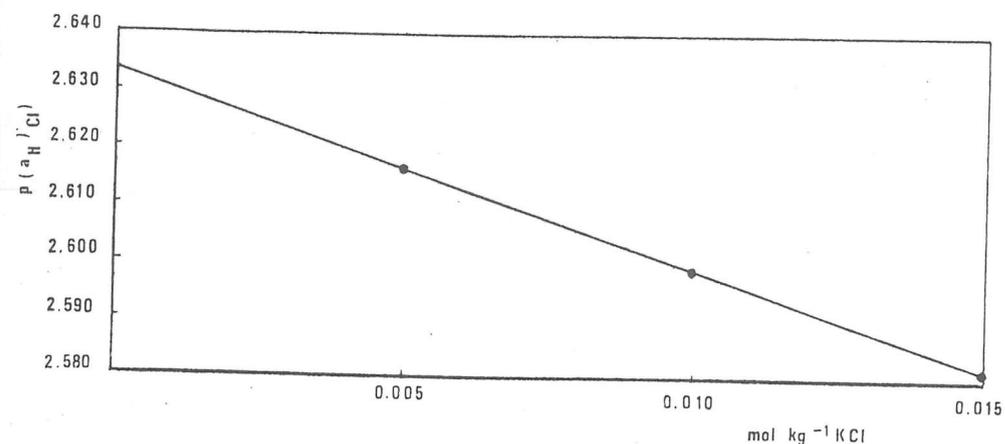


FIGURE 1. Variation of calculated (equation 3)  $p(a_{H^+} \gamma_{Cl})$  values of 0.01 m  $H_3Cit$  solutions with addition of KCl.

An experimental study by Bates *et al.* [2] of a similar system with application of equation (1) produced a straight line of positive slope, Fig. 2.

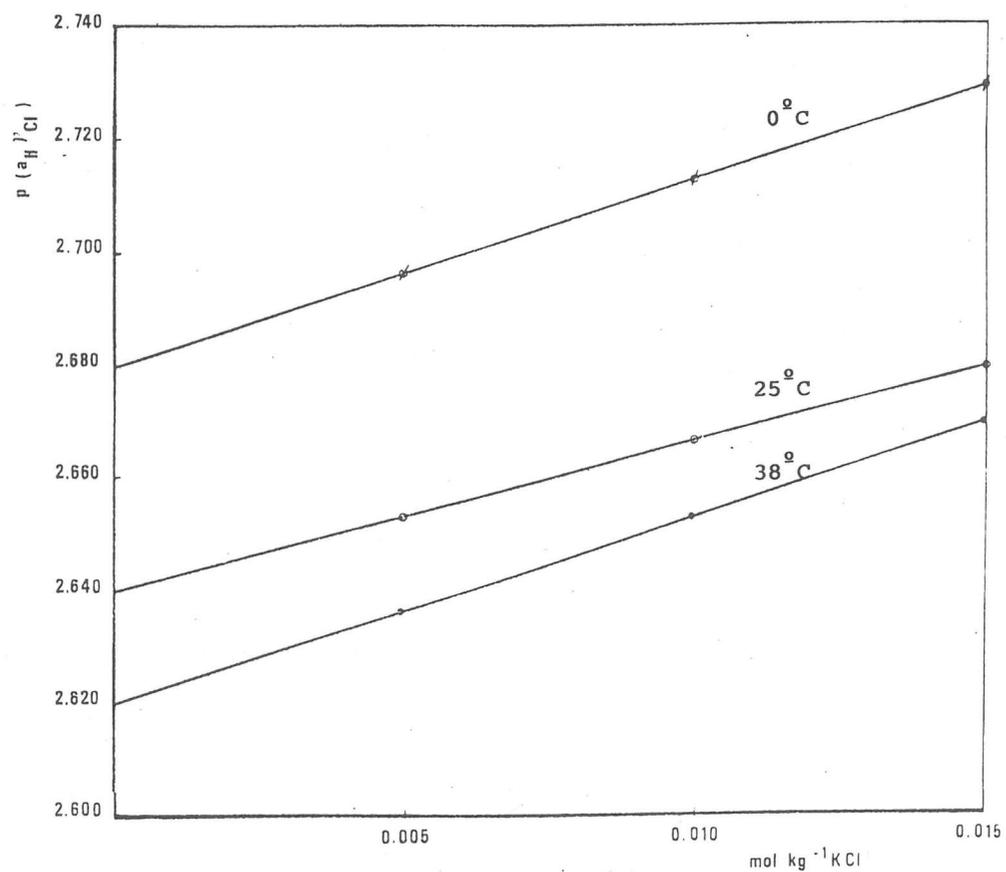


FIGURE 2

Variation of experimentally accessed (equation 1)  $p(a_{H^+}\gamma_{Cl^-})$  values of 0.01 m  $H_3Cit$  solutions with added KCl.

For 0.1 mol  $dm^{-3}$   $KH_2Cit$  solutions, both calculated and experimental [2] results produce negative slopes, as can be seen from Table 2, Fig. 3 and Fig. 4.

TABLE 2. Calculated (equation 3) values of  $I$ ,  $\log \gamma_1$  and  $p(a_{H^+}\gamma_{Cl^-})$  for 0.1 m  $KH_2Cit$  solutions with added KCl

KCl(m)	I	$\log \gamma_1$	$p(a_{H^+}\gamma_{Cl^-})$
0	0.115	-0.11495	3.830
0.005	0.120	-0.11644	3.827
0.01	0.125	-0.11801	3.824
0.015	0.130	-0.11953	3.821

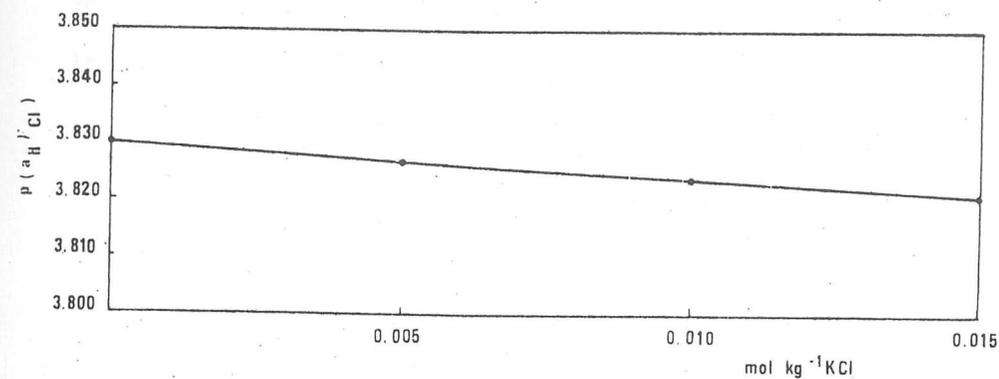


FIGURE 3

Variation of calculated (equation 3)  $p(a_{H^+}\gamma_{Cl^-})$  values of 0.1 m  $KH_2Cit$  solutions with addition of KCl.

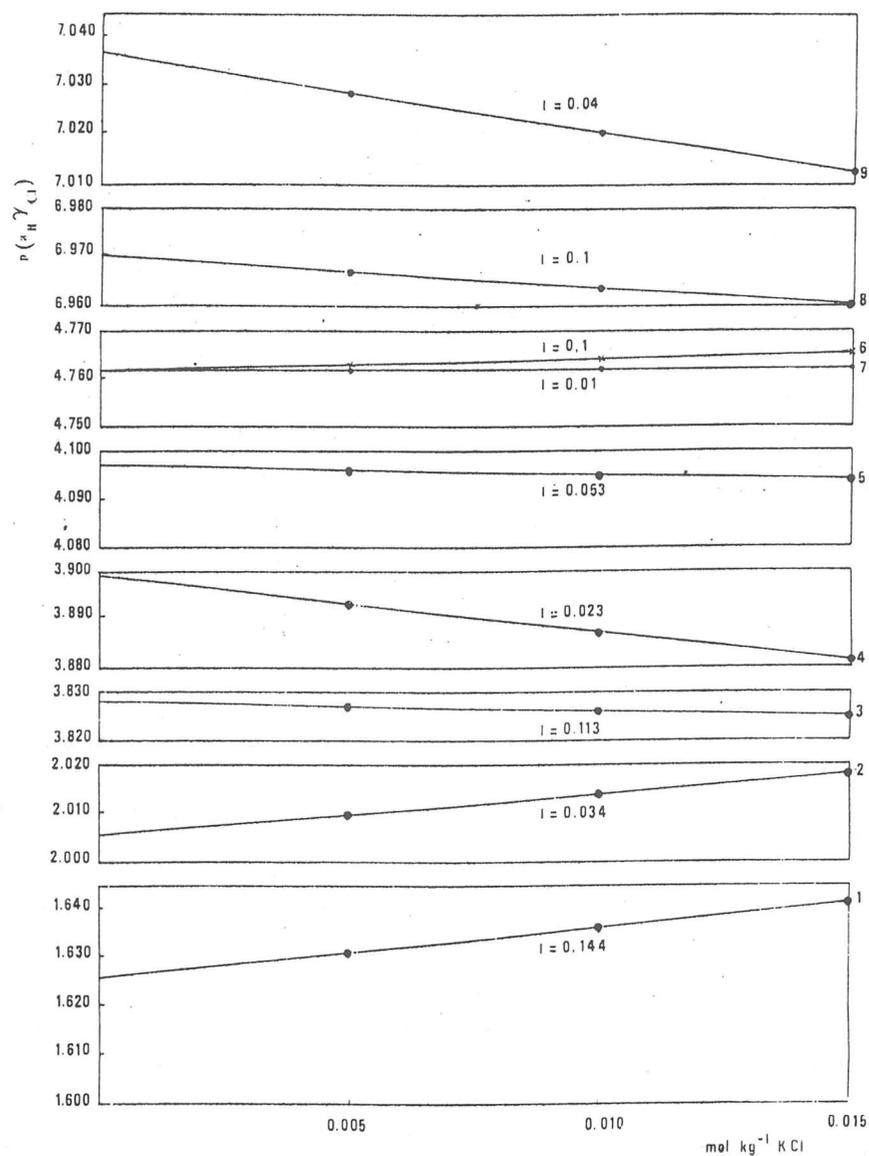


FIGURE 4

Variation of experimentally accessed [2]  $p(a_{H^+} \gamma_{Cl^-})$  values of various buffer solutions, at 25 C, with addition of KCl

- |   |  |
|---|--|
| 1. 0.1 m $\text{KH}_3(\text{C}_2\text{O}_4)_2$                      | 2. 0.02 m $\text{KH}_3(\text{C}_2\text{O}_4)_2$                    |
| 3. 0.1 m $\text{KH}_2\text{Cit}$                                    | 4. 0.02 m $\text{KH}_2\text{Cit}$                                  |
| 5. 0.05 m KH Phthal.  | 6. (0.1 m/0.1 m) HAc/NaAc  |
| 7. (0.01 m/0.01 m) HAc/NaAc   | 8. 0.025m/0.025m) $\text{KH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ |
| 9. (0.01 m/0.01 m) $\text{KH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ |  |

Observation of Fig. 4 shows that bigger disagreements occur for mixtures of salt and acid at higher ionic strengths.

While calculated values (equation 3) always produce a line of negative slope, experimental studies of the citrate buffer [3] from various suppliers (A,B,C) produced slopes that ranged from positive to negative, Fig. 5, thus arising the question of interpretation.

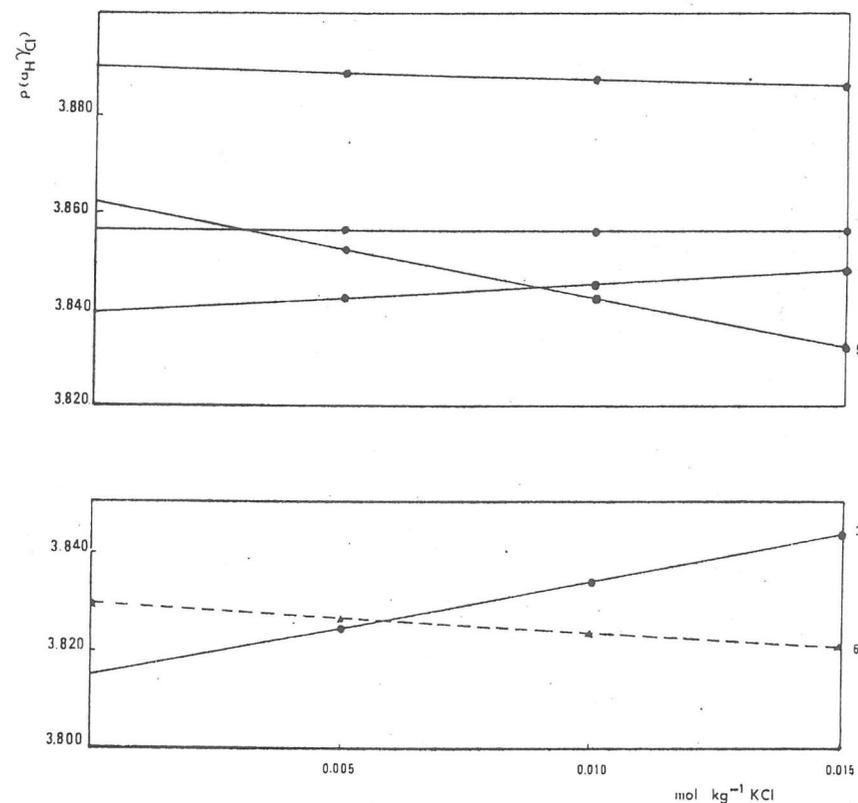


FIGURE 5

Variation of experimentally accessed (1,2,3,4,5) and calculated (6)  $p(a_{H^+} \gamma_{Cl^-})$  values of citrate buffer solutions from various suppliers (A,B,C)

- |                                       |                                       |
|---------------------------------------|---------------------------------------|
| 1. 0.02 m $\text{KH}_2\text{Cit}$ (A) | 2. 0.05 m $\text{KH}_2\text{Cit}$ (A) |
| 3. 0.1 m $\text{KH}_2\text{Cit}$ (A)  | 4. 0.1 m $\text{KH}_2\text{Cit}$ (B)  |
| 5. 0.1 m $\text{KH}_2\text{Cit}$ (C)  | 6. 0.1 m $\text{KH}_2\text{Cit}$      |

This could be explained in terms of displacement in the equilibrium conditions, promoted by the addition of KCl, with consequent increasing of the buffer ratio  $\frac{m_A}{m_{H_2A}}$ , not previously accounted for.

Evaluation of pH values for  $KH_2Cit$  buffer system eventually contaminated with  $H_3Cit$  is, therefore, bound to suffer from unprecise extrapolation. Nevertheless, comparison of calculated and experimental results proved to be a good indication of acid contamination and has led to the development of a methodology for the purification of the solid reagent [4].

**REFERENCES**

[1] M.J. Guiomar H.M. Lito, M. Filomena G.F.C. Camões, M. Isabel A. Ferra, Arthur K. Covington, *Anal. Chim. Acta*, **239**, 129 (1990).

[2] R.G. Bates, G.D. Pinching, E.R. Smith, *J. Res. Nat. Bur. Stand.*, **45(5)**, 418 (1950).

[3] M.J. Guiomar H.M. Lito, M. Filomena G.F.C. Camões, "Estequiometria em Soluções de dihidrogenocitrato de potássio", 7<sup>o</sup> Encontro Anual da Sociedade Portuguesa de Química - Lisboa, Julho 1984.

[4] M.J. Guiomar H.M. Lito, M. Filomena G.F.C. Camões, "Soluções padrão de tampão citrato", 3<sup>o</sup> Encontro da Sociedade Portuguesa de Electroquímica, Faro, Outubro de 1987.

**ANODIC OXIDATION OF DMAB AND INFLUENCE OF ADDITIVES IN ELECTROLESS PLATING**

A. P. Ricardo\* and L. M. Abrantes\*\*

\* DER, Azinhaga dos Lameiros à Estrada do Paço do Lumiar, 1699 Lisboa Codex, PORTUGAL

\*\* CECUL (INIC), Department of Chemistry, Faculty of Sciences, 1294 Lisboa Codex, PORTUGAL

The electrochemical nature of electroless plating is widely accepted [1,2]. The electrode processes involve simultaneously the anodic oxidation of a reductant and the cathodic metal deposition and these partial reactions may proceed by several steps.

In connection with the catalytic activity of the substrates there is experimental evidence for considering the reductant oxidation the dominant factor in electroless process [3,4].

In this work specpure nickel and cobalt were used to study the electrochemical behaviour of dimethylamine borane (DMAB) in acetate containing solutions of slightly alkaline pH. The effect associated to the presence in the electrolyte of thiourea and N-methylthiourea was also considered.

At a given concentration of the reductant, Ni and Co present different behaviours, as can be seen by the evolution of the electrode open-circuit potential with time, illustrated in figure 1. However, as the concentration of DMAB increases the "induction" period is shorter for Co and Ni substrate can present catalytic activity, which suggests an interaction between the substrate and the reducing agent - e. g. adsorption as a first step.

A subsequent formation of radicals is likely to occur as well as its oxidation, reactions 1 and 2.

