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DETERMINATION OF STABILITY CONSTANTS USING ASV TECHNIQUE (SURFACE CONCENTRATION EFFECT)

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ABSTRACT

The surface concentration effect of the metal ion during the stripping step of ASV, in a complexing medium, is discussed in terms of determination of stability constants, from the results for Pb(II) + TETA system.

Subsequently stability constants of Cd(II) + carboxy-phenyliminodiacetic acid, phenylmethyliminodiacetic acid, pyridine-2,6-dicarboxylic acid and pyridine-2-carboxylic acid have been determined and the values compared with those obtained by other techniques.

Portugaliæ Electrochimica Acta, 3 (1985) 293-310

1. INTRODUCTION

Anodic stripping voltammetry is a very useful technique for the determination of heavy metals in natural waters, due to its very low detection limit[1,2]. From this point of view it is, in fact, the most convenient technique within the voltammetric methods, since during the electrolysis step the metal is preconcentrated in the electrode, before the anodic voltammetric step. However, this combination of methods, responsible for the high sensitivity of the technique, can introduce some limitations owing to the volume concentration of the metal at the electrode surface during the stripping step, which is higher than in the bulk solution. So if ligands are present in solution together with metals, the high ratio C_L/C_M necessary for the application of the voltammetric methods to labile complexes may not exist at the electrode surface during the stripping step, even when this happens in the bulk of the solution. This surface effect is discussed in this paper in terms of determination of stability constants.

2. EXPERIMENTAL

Solutions were prepared from de-ionised water and reagent grade chemicals (purity > 98%). The solutions of the metal in the presence of the ligand were buffered at pH ~7.5 - 8.5. In the absence of the ligand lead solutions were used at pH ~ 5.5 and cadmium solutions at pH ~ 5-7 to prevent the hydrolysis of the metal ion[3].

The measurements were done at 25.0°C in 0.10 M KNO_3 for the system Pb(II) + triethylenetetramine (TETA) and 0.10 M Na ClO_4 for the other systems. The pH of each solution in the cell was measured with an error < 0.01 units of pH.

Dissolved oxygen was removed by bubbling purified nitrogen

through the solutions.

The ASV voltamograms for the system Pb(II) + TETA were obtained with a Tacussel PRG5 polarograph and for the other systems with a PAR Model 174. The working electrode was a METRHOM EA-290 hanging mercury drop. The solutions were stirred during the deposition step with a teflon magnetic bar fitted to the internal bottom diameter of the cell to prevent any lateral movement. The potential applied during this step was E_d = -0.700 V for the Pb(II) system and E_d = -0.900 V for the Cd(II) systems. Before the anodic scan the solution was maintained unstirred for 30 sec.

The radius of the Hg drop was determined by weighing a fixed number of drops in solutions.

The average thickness of the diffusion layer - δ - in the solution during the deposition step, was calculated my measuring the average value of the deposition current - $\bar{i}_d$ - in an uncomplexing solution[4]:

$$\delta = nFS\, D_{pb}\, C_{Pb} / \bar{i}_d$$

where n = 2, F = 96500 C, $D_{Pb} = 8.3 \times 10^{-6} cm^2/s$, $C_{Pb} = 10^{-4} M$

S = surface area of the Hg drop.

The reproducibility of ASV results is largely affected by experimental parameters and so it is very important to keep them constant.

For the determination of the stability constants of cadmium systems by ASV, the metal concentration in solution was kept constant at $(5-10) \times 10^{-7} M$ and C_L/C_M varied between 80 and 1000. The experimental parameters were:

r_o = 0.040 cm; = 1.7 x 10^{-3} cm; t_d = 15 - 180 s; scan rate = 10 mV/s.

3. RESULTS AND DISCUSSION

In order to study the influence of the surface effect in the determination of the stability constants by ASV and how to avoid this effect, the system Pb(II) + TETA has been chosen since this ligand forms a very stable ML complex that behaves reversibly and is labile within the time scale of the anodic stripping technique.

SURFACE CONCENTRATION EFFECT

a) Qualitative interpretation

The surface concentration of the metal ion in the stripping step has a significant influence in the peak parameters of the ASV curve in a complexing medium where labile complexes are being formed.

A qualitative description of the shape of ASV curves should then be given in terms of the metal ion volume concentration at the electrode surface, C_M^o, which increases with the deposition time, t_d:

1) For very low t_d values and high ligand concentrations, $C_L^o >> C_M^o$, $(C_L^o - |ML|^o) \sim C_L^o$ and $C_L^o \sim C_L$. The subscript o refers to the volume concentration at the surface and C_L represents the total ligand concentration in the bulk solution.

In these conditions the DeFord-Hume's method[5], applied to labile and reversible systems, initially developed for DC polarography, could also be applied to ASV, $i_p^M/i_p^{M+L} = 1$ since $D_M \sim D_{ML}$[6]:

$$\Delta E_p = E_p^M - E_p^{M+L} = \frac{RT}{nF} \ln ((i_p^M/i_p^{M+L}) (1 + \beta_{ML} C_L/\alpha_H)) \qquad (1)$$

where: i) M and M+L stand respectively for the uncomplexing and complexing medium, ii) i_p and E_p represent the current and the potential of the peak, iii) $\alpha_H = 1 + \beta_1^H |H| + \beta_2^H |H|^2$, iv) the other letters have their usual meaning.

2) For low deposition time where $C_L > C_M^o$ but C_L/C_M^o is significantly smaller than C_L/C_M, the peak is shifted to more positive values because of the lower C_L/C_M^o ratio observed, and it is broadened, due to the decrease of C_L/C_M^o ratio during the rising part of the ASV voltagram (Fig. 1, curve 1).

3) For higher deposition times (Fig. 1, curve 2 and 3) where $C_M^o > C_L$, a shoulder of constant height can be noticed which remains at the same potential value with the increase of t_d, while the peak increases and is shifted to potential values closer to the peak of the non complexed metal ion. The shoulder can be attributed to the reoxydation of M under the ML form; its constant height is due to the saturation of L at the electrode surface, while the peak is due to the reduction of the excess of the free metal ion ($C_M^o > C_L$). It is important to note that in Fig. 1 the normalised height of the shoulder, $i'_{sh} = i_{sh}/t_d$, decreases when t_d increases because i_{sh} is a constant value.

b) Quantitative interpretation

In order to quantify this surface effect we should be able to determine C_M^o at each deposition time. The following equation was deduced for the hanging mercury drop electrode (HMDE) in reversible conditions, in the absence of ligand, for a deposition potential (E_d) on the plateau of the reduction wave and for scan rates of the stripping step, in such a way that M(Hg) = const. inside the mercury drop (v > 5 mV/s)[7]:

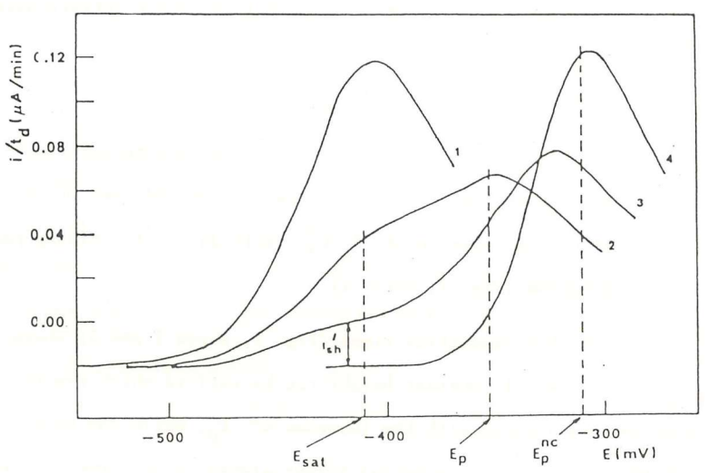

Fig. 1 - Normalised ASV voltamograms of lead ion (C_M= 1.00 x 10^{-6}M in the presence of TETA (C_L= 0.98 x 10^{-4}M) - curves 1, 2, 3 respectively, with t_d = 1; 7; 25 mn -, and in its absence - curve 4 - ; $i'_{sh} = i_{shoulder}/t_d$.

$$\frac{C_M^o}{C_M} = \frac{1}{K} \cdot \frac{D_{ox}^{1/2} D_r^{1/2}}{r_o \delta} \times t_d \qquad (2)$$

where r_o is the radius of the mercury drop, δ is the thickness of the diffusion layer, D_{ox} and D_r are the diffusion coefficients of the metal in solution and in the mercury, C_M^o is the concentration at the electrode surface for the peak potential, and K is a constant value theoretically equal to 0.44[7].

From this equation and using typical parameters it is possible to estimate that $C_M^o/C_M = 20\ t_d$, t_d being expressed in minutes. This

means, therefore, that for a typical deposition time of 3 minutes the metal concentration of the electrode surface can be 60 times as high as the value of the bulk of the solution.

In order to see if expression (2) can be applied in a complexing medium where labile complexes are being formed, the validity of the last expression was checked for the system Pb(II) + TETA[6]. Experimentally, one cannot directly measure C_M^o, but the critical deposition time (t_c) corresponding to $C_M^o \simeq C_L$ can be determined superimposing i_{sh} value on the plot of i_p vs t_d for the metal (considering $D_{ML} \simeq D_M$), where i_{sh} is the height of the shoulder (Fig. 1). Taking into account this definition and assuming that eq. (2) is still valid in the presence of ligands, we have, replacing C_M^o in eq. (2) by C_L and t_d by t_c:

$$C_L/C_M = \frac{1}{K} \cdot \frac{\sqrt{D_{ox} D_r}}{r_o \delta} \cdot t_c \qquad (3)$$

where $D_{ox} = D_{ML} \simeq D_M$.

In fact, a linear relationship between t_c and the ratio $C_L\ r_o\ \delta/C_M$ is obtained experimentally (Fig. 2), for different ligand and metal concentrations, different radii of mercury drops and for some values of stirring rates (experimental conditions are given in Table I).

The linearity observed proves that experimental parameters affect, in a similar way, C_M^o value in a complexing or uncomplexing medium. In the complexing medium an experimental value $K = 0.61 \pm 0.04$ is found that is of the same order of magnitude as the theoretical result obtained in the absence of ligand.

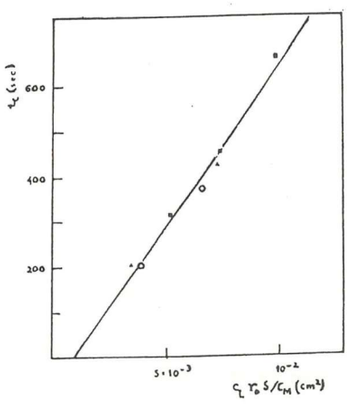

Fig. 2 - Influence of the experimental parameters δ (■), r_o (o) and C_L/C_M (▲) on the critical deposition time t_c. Experimental conditions are given in Table I.

Table I

Values of t_c found for different values of the experimental parameters r_o, δ and C_L/C_M

r_o (cm)	δ (cm)	C_L/C_M	t_c (min)
0.055	1.2×10^{-3}	98	6.2
0.044	1.2×10^{-3}	136	7.1
0.044	1.2×10^{-3}	98	5.2
0.044	1.2×10^{-3}	65	3.4
0.044	1.7×10^{-3}	98	7.6
0.044	2.3×10^{-3}	98	11.0
0.032	1.2×10^{-3}	98	3.4

The validity of expression (2) in the presence of the ligand can also be observed if one compares the experimental values of the peak potential (E_p) of the voltamograms obtained by ASV for several deposition times, with the value calculated from DeFord Hume's method[5]:

$$(E_p)_{M+L} = (E_p)_M - \frac{RT}{nF} \ln (1 + \beta_{ML} |L|^o) \qquad (4)$$

where the free concentration of the ligand at the electrode surface, $|L|^o$, is obtained from the mass balance equations of the total concentration of ligand and metal at the electrode surface ($C_L^o = C_L$ and C_M^o given by eq. (2) with K = 0.61). A reasonable agreement within the experimental error ($\Delta E < 5$ mV) (Table II), is observed for low values of t_d ($C_L^o > C_M^o$) when only one peak appears - see Fig. 1 -, and for high values of t_d ($C_M^o < C_L^o$). For intermediate values (C_L/C_M^o between 1 and 0.2) for which the height and the potential of the shoulder are close to the peak, the measurement of the peak potential has a big error.

Table II - Experimental and calculated peak potentials E_p for different deposition times

td(mn)	C_L/C_M^o	$E_p$exp(V)	$E_p$calc.(V)	$E_p$exp - $E_p$calc. (mV)
0.5	8	-0.410	-0.413	+3
1	4	-0.407	-0.411	+4
2	2	-0.402	-0.406	+4
7	0.5	-0.350	-0.324	-26
15	0.25	-0.330	-0.318	-12
17.5	0.2	-0.326	-0.317	-9
25	0.15	-0.320	-0.316	-4

DETERMINATION OF STABILITY CONSTANTS BY ASV

It is important to develop new methods which allow the determination of stability constants from techniques that could be used for low metal concentration, as is generally the case in natural waters.

In this context ASV technique seems to be one of the best because it can detect metal concentration as low as 10^{-9}M.

If the complexes are labile during the stripping step the peak potential should change with the ligand concentration for the same deposition time or with the deposition time for the same ligand concentration. Depending on the C_L/C_M^o ratio, two cases should be considered:

1) If $C_L >> C_M^o$ ($|ML|^o << C_L$). The stability constant could be obtained from equation 1 as was discussed in the previous section.

From eq. (2) it can be seen that this condition is only obtained if $C_L/C_M \geq 1000$, assuming $C_M^o \leq 5\% C_L$, and using typical experimental parameters ($r_o = 0.040$ cm; $\delta = 1.2 \times 10^{-3}$cm, $t_d = 3$ minutes, $D_{ox} \sim D_r \sim 10^{-5}$ cm^2/s).

2) If $C_L > C_M^o$ but $|ML|^o$ is not negligible in comparison with C_L, the peak potential shifts to more positive values with the increase of t_d, and a linear plot of E_p vs t_d is experimentally found for $t_d < t_c$ (Fig. 3). This could be anticipated from equation (4) if:

a) $|M|^o << |ML|^o$ (which is valid for $t_d < t_c$ and strong complexes).

b) $C_L^o \sim C_L$ and C_M^o given by equation (2).

c) $t_d << t_c$.

Indeed, in these conditions one obtains a linear relationship between ΔE_p and t_d:

$$\Delta E_p = \frac{RT}{nF} \ln (\beta_{ML} C_L/\alpha_H^o) + \frac{RT}{nF} \frac{1}{K} D_{ox}^{1/2} D_r^{1/2} C_M t_d/(\delta R_o C_L) \quad (5)$$

and from the intercept $(\Delta E_p)_{t_d=0} = \frac{RT}{nF} \ln (\beta_{ML} C_L/\alpha_H^o)$ ($\alpha_H^o = \alpha_H$ if the medium is well buffered) the stability constant β_{ML} can be easily determined.

The extrapolation to $t_d = 0$ signifies the elimination of the surface effect, which is negligible from a t_d value depending on the ratio C_L/C_M.

The mean value of log β_{ML} determined by this method for the system Pb(II) + TETA from the experimental conditions of Table I and Fig. 3 is log $\beta_{ML} = 10.25 \pm .04$ which is in good agreement, within

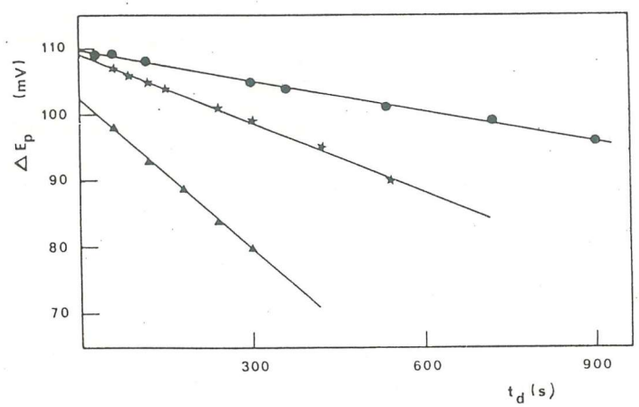

Fig. 3 - Change of ΔE_p with t_d, for $t_d < t_c$.
Experimental conditions:
$R_o = 0.040$ cm
(●) $C_L/C_M = 1225$; $C_L = 4.9 \times 10^{-4}$M; pH = 7.80; $\delta = 1.2 \times 10^{-3}$cm
(★) $C_L/C_M = 306$; $C_L = 4.9 \times 10^{-4}$M; pH = 7.81; $\delta = 1.2 \times 10^{-3}$cm
(▲) $C_L/C_M = 98$; $C_L = 0.98 \times 10^{-4}$M; pH = 8.05; $\delta = 1.7 \times 10^{-3}$cm

the experimental errors, with the value obtained by DC voltammetry with a HMDE: $\log \beta_{ML} = 10.19 \pm .03$.

Hence, from the study of Pb(II)+ TETA system we can conclude that, in order to avoid the surface effect, the stability constants can be determined by DeFord and Hume's method after extrapolation of E_p at $t_d = 0$.

This study was extended to other systems with Cd(II) and some chelating groups of humic or fulvic acids found in natural waters: carboxyphenyliminodiacetic, phenylmethyliminodiacetic, pyridine-2--carboxylic and pyridine-2,6-dicarboxylic acids. The stability constants have also been determined using different analytical techniques besides ASV like differential pulse polarography, normal pulse polarography with reversed pulse mode and potentiometry.

The comparison of the values obtained by DPP and ASV is important since in the first technique there is only the reduction step whereas in ASV both reduction and oxidation steps occur; if the values obtained by both techniques agree, it may be inferred that a slow step does not exist in the electrochemical or in the chemical reaction during the electrode process, either in the deposition step or in the stripping one. On the other hand, the comparison of the stability constants obtained by pH titration and ASV is also important, since the first technique, which needs higher concentration in solution, is generally more accurate and precise. Since voltammetric techniques use a high excess of ligand ($C_L > 20\ C_M$), complexed species with higher ratio of ligand to metal ions might be formed compared with the ones formed in potentiometry. However, in our systems the same species are found in the samples whatever the technique used, except for the system Cd(II) + pyridine-2,6--dicarboxylic in which under potentiometric conditions the ML and ML_2 species are formed whereas with ASV only the ML_2 species have been experimentally detected.

It was shown that the linearity of the E_p vs t_d plot should be valid for small values of t_d and for a system with one strong complex form, the slope being proportional to C_M/C_L for the same experimental conditions.

If there are two strong complexes in solution, ML and ML_2, ΔE_p becomes:

$$\Delta E_p = \frac{RT}{nF} \ln (1 + \beta_{ML} |L|^o + \beta_{ML_2} |L|^{o2})$$

where $|L|^o$ can be determined as a function of t_d from the mass balance equations (assuming $C_L^o = C_L$ and C_M^o given by equation (2)), and so a curve is expressed from ΔE_p vs t_d. However, replacing the experimental parameters for the values used in this work, and the stability constants for the values obtained by potentiometry, one can find that the calculated points $(\Delta E_p, t_d)$, for small values of t_d, fit a straight line withing the experimental errors. So one should expect at least a rough linear relationship ΔE_p vs t_d for all the systems studied in this work, provided small t_d values are used.

This behaviour has been found for the systems Pb(II) + TETA and Cd(II) + carboxyphenyliminodiacetic acid. In the other systems the slope increases for higher concentrations of ligand and a break point is sometimes observed for small values of td (td < 3 mn), as can be seen in Fig. 4 where two segments are obtained for td < 1 min and 1 < td < 3 min.

This observation must be compared to the results of adsorption studies on the Hg drop: it has been noticed[9] that there is no adsorption for Pb(II) + TETA and Cd(II) + carboxyphenyliminodiacetic system

but a strong evidence of adsorption is observed with the complexes Cd(II) and phenylmethyliminodiacetic, pyridinedicarboxylic and pyridinecarboxylix acids. In fact, using the NPP technique with direct scan, it has been noticed that for the last three systems the polarograms present a typical adsorption maximum at the beginning of the wave[10], this effect being minimized with reverse pulse mode. This adsorption can be anticipated due to the higher affinity of neutral species to the mercury interface, since the ML species formed in system no. I (see Table III) is negatively charged, whereas the ML species formed with systems nos. II and III and ML_2 with the system IV have no charge. It is then likely that the difference between the plots E_p vs t_d in Fig. 4, compared with those of simple labile systems, is due to adsorption problems.

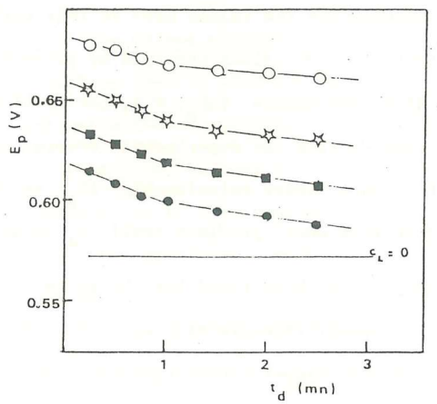

Fig. 4 - Changes in the peak potential for small values of t_d, for the system Cd(II) + phenylmethyliminodiacetic acid.
$C_{Cd} = 5 \times 10^{-7}$M
$C_L = 30 \times 10^{-6}$M
$C_L = 50 \times 10^{-6}$M
$C_L = 148 \times 10^{-6}$M
$C_L = 493 \times 10^{-6}$M

From Table III it can be seen that in general DPP is more affected by adsorption problems since the stability constants could not be determined for the cadmium complexes with two of the ligands. However, the adsorption with these systems becomes more difficult in RNPP because an adequate initial potential can be used where the adsorption is made difficult. Comparing the results obtained by potentiometry, ASV and RNPP (E_d value in ASV being coincident with the E_i potential of RNPP and equal to -0.9 V), it can be noticed from Table III that the values obtained by the last two techniques are slightly higher than potentiometric values, which can be considered more accurate. This can be due to the fact that the adsorption effects on the mercury may not be completely eliminated in ASV and RNPP techniques. The results obtained with the first technique are closer to the potentiometric values probably due to the lower concentration of the ligands used in ASV.

Both to understand and to avoid the kind of adsorption present in these systems, a study is being undertaken by RNPP and a.c. polarography, analysing the effects of the initial potential, ligand concentration and drop time, as well as the pulse duration in the first technique.

CONCLUSIONS

ASV technique can be used for the determination of stability constants using DeFord-Hume's method with the peak potential of the complexed form, if $C_L/C_M > 1000$ and deposition times are less than 3 min., for typical experimental parameters ($r_o = 0.04$ cm; $\delta = 1.2 \times 10^{-3}$cm; $D_{ox} \sim D_r \sim 10^{-5}$cm^2 s^{-1}).

For lower C_L/C_M values the determination of stability constants

Table III

Stability constants obtained by ASV, extrapolating E_p for $t_d = 0$, and by other analytical techniques, at 25°C and 0.10 M $NaClO_4$

System		ASV	pH titration	NPP reverse scan	DPP
Cd(II)--					
Carboxy-phenyl-imino-diacetic acid.	I log β_{ML}	7.15	7.31	7.11	not* possible
Phenyl-methyl-imino-diacetic acid	log β_{ML} II log β_{ML_2}	7.0 11.45	6.16 11.26	8.3 12.0	adsorption "
Pyridine dicar-boxylic acid	log β_{ML} III log β_{ML_2}	- 11.45	6.36 10.90	- 11.47	" "
Pyridine car-boxylic acid	log β_{ML} IV log β_{ML_2}	4.6 8.4	4.36 7.99	4.8 9.0	4.5 8.3

* Quasi-labile system with the reduction peaks of the free metal after dissociation and of the complex itself very close to each other.

involves a previous extrapolation of E_p vs t_d curve for $t_d = 0$ in order to avoid the surface concentration effect. This extrapolation can be done within the experimental errors since a linear relationship should be expected between ΔE_p and t_d for small values of t_d.

The stability constants calculated by ASV for the system Pb(II) + TETA and Cd(II) + phenylmethyliminodiacetic acid agree with those obtained by other techniques.

Deviations from the above mentioned linearity as well as the higher values obtained for stability constants by ASV and RPP compared with potentiometric ones, in the systems Cd(II) + benzyliminodiacetic, pyridine-2,6-dicarboxylic and pyridine-2-carboxylic acids, might be due to adsorption problems of the ligands or the complexes on the mercury drop.

Acknowledgement: This work was partially supported by Junta Nacional de Investigação Científica e Tecnológica under the research contract nº 315.81.57.

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(Received 13 September 1985
in revised form 2 April/1986)

ELÉCTRODO SELECTIVO PARA CATIÃO POTASSIO COM SENSOR IMOBILIZADO EM PVC APLICADO A UM SUPORTE DE RESINA CONDUTORA*

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RESUMO: Descreve-se uma nova técnica de construção de eléctrodos selectivos de membrana de PVC que consiste na formação desta sobre um suporte de resina condutora epoxi à base de prata. A técnica foi usada na montagem de um eléctrodo para catião potássio em que se utilizou o sensor Corning 477317. O estudo das características de resposta do eléctrodo mostrou que este apresenta qualidade semelhante à do eléctrodo de membrana de PVC de construção convencional (com solução e eléctrodo de referência internos) com o mesmo sensor, mas durabilidade apreciàvelmente superior. Discutem-se as vantagens e desvantagens da técnica proposta sobre as técnicas de construção de eléctrodos de membrana de PVC anteriormente usadas (preparação de eléctrodos convencionais ou de "fio recoberto").

ABSTRACT: Potassium Ion Selective Electrode with a PVC Membrane Applied to a Conductive Epoxy Support. A new technique for the construction of "all solid state" PVC membrane electrodes which consists of direct formation of the membrane on a support of silver loaded conductive epoxi is described. The response characteristics of a potassium electrode with the Corning 477317 sensor prepared by this technique are presented. The electrode shows performance similar to the conventional (with internal solution) electrode with the same sensor, but longer durability. The advantages and shortcomings of the present construction technique over the procedures previously described for the assembly of PVC membrane electrodes (of conventional or "coated-wire" types) are discussed

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* Apresentado, em parte, à Quarta Reunião Nacional de Electroquímica, Braga,1983, Comunicação C30.4 (ref.[1]).