The quality of the calibration model obtained, was evaluated by plotting the predicted concentrations against the actual concentrations for each standard (Fig. 2). The correlation coefficients found by PLS model, with 2 factors, are 0.996 and 0.998 for calibration of Cd and In, respectively, indicated a good agreement between the actual and predicted concentrations.

APPLICATIONS

The calibration model was applied to the determination of In and Cd in artificial samples in order to verify its predictive ability. The results obtained are summarized in Table 2.

Table 2 – Simultaneous determination of In and Cd in artificial mixtures.

Artificial Mixtures	Cd^{2+} (µg/L)		Relative Error (%)	Recovery (%)	In^{3+} (µg/L)		Relative Error (%)	Recovery (%)
	Actual	Predicted			Actual	Predicted		
I	50.0	54.4	8.8	108.8	150.1	146.1	-2.7	97.4
II	100.2	107.9	7.7	107.7	200.2	195.7	-2.2	97.7
III	100.0	95.6	-4.4	95.6	25.0	21.2	-15.2	84.8
IV	247.8	229.2	-7.5	92.5	0	-1.0	—	—
V	150.0	150.1	0.1	100.1	49.9	49.8	-0.2	99.8

The results indicate that the magnitude of the error depends greatly on the relative amount of each component in the mixture: the error is large for the minor component amount.

On the other hand, high relative errors are observed in the determination of Cd. This is probably due to the relatively large differences in sensitivity of the analytical signal. Because the sensitivity of the voltammetric peak of Cd is smaller than that of In (Fig. 1), the contribution of Cd for the overall analytical signal is, in some way, masked by the In.

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EFFECT OF THE TEMPERATURE ON THE RESPONSE OF ALL-SOLID-STATE NONACTIN AMMONIUM ISE's WITH PVC MEMBRANES APPLIED TO GRAPHITE FILLED EPOXY SUPPORTS

Júlia M.C.S. Magalhães and Adélio A.S.C. Machado[1]

LAQUIPAI, Faculdade de Ciências, R. Campo Alegre 687, P4150 Porto, Portugal

ABSTRACT: Preliminary results of a study of the effect of the temperature on the response of all-solid-state ammonium ISE's prepared by casting PVC membranes with nonactin on supports of graphite/epoxy composites with up to 60% of graphite are presented. The study showed that: (i) the conductive suppport must contain at least 40% of graphite to produce ISE's with adequate response characteristics; and (ii) the variation of the percentage of graphite between 40 and 60% has no influence on the slope and potential temperature coefficients and on the hysteresis curves of the electrodes.

RESUMO: Apresentam-se resultados preliminares do estudo do efeito da temperatura na resposta de eléctrodos selectivos sensíveis a catião amónio construídos por aplicação de membranas de PVC, com sensor de nonactina, sobre suportes condutores constituídos por misturas de grafite com uma resina epoxídica, com percentagens de grafite até 60%. Este estudo mostrou que: (i) o suporte condutor deve conter pelo menos 40% de grafite para se obterem ESI's com características de resposta adequadas; e (ii) a variação da percentagem de grafite no suporte condutor entre 40 e 60%, não influencia os coeficientes térmicos de declive e de potencial nem as curvas de histerese dos eléctrodos.

KEYWORDS: Temperature properties; conductive epoxy electrodes; all-solid-state electrodes; ammonium nonactin PVC electrodes; graphite/epoxy composite.

INTRODUCTION

The differentiation with respect to the temperature of the response equation of an ion selective electrode (ISE) shows that the effect of the temperature on the electrode response is intrinsically complex [1]. Moreover, when all-solid-state ISE's are considered, the variety of processes involved both in the inner set of solid conductors and in the membrane/support interface isresponsible for further complexity. Indeed, previous work [2 and references therein] showed that the effect of the temperature on the response of all-solid-state ISE's with conductive epoxy supports depends on a large variety of factors, for instance, the type of membrane, the nature of the internal contact, the metal used as conductive filling of the epoxy, the sensor system, etc. The purpose of such work was to improve the construction procedure of electrodes with conductive epoxy supports to bring the concentration of the isopotential point into the operational range. This purpose was not reached because the

[1] Author for correspondence

complexity of the behaviour of the electrodes made impossible to obtain systematic relations between the constructive parameters and the position of the isopotential point. Therefore, it was decided to develop further studies to identify the extension in which each constructive parameter affects the influence of the temperature on the response of the electrodes.

This paper presents preliminary results obtained in a study of the effect of the relative content of graphite in the support on the temperature behaviour of the response of all-solid-state nonactin ammonium ISE's prepared by casting PVC membranes on conductive graphite/epoxy composites. The study involved the preparation of electrodes with supports containing 10-60 % of graphite dispersed in a non conductive epoxy and measurements of their responses in the temperature range between 10-50 °C, including calibrations and hysteresis curves.

EXPERIMENTAL

Equipment and reagents

For the calibration of the ISE's, an automatic system constituted by a PC (Compac Prolinea 3/25s), a microburete (model Microbu 2030 from Crison) and a pHmeter (Micro pH 2002 from Crison) was used.

The hysteresis curves of the ISE's were obtained with an automatic system constituted by a PC (Compac Prolinea 3/25s), equipped with a Lab Master DMA multifunction card, a high impedance circuit box, a thermoregulator (model TU-16D from Techne Inc.) and a double wall vessel with 50 ml of capacity (Methrom). This syste with 50 ml of capacity (Methrom). This system, which was described in detail elsewhere [3], allows parallel determinations on up to five electrodes.

The reference electrode was a double junction Orion 90-02-00 electrode, with lithium acetate in the external compartment. The reagents
for the preparation of the solutions were of p.a. grade or equivalent.

Ion selective electrodes

The membranes were constituted by 3% of nonactin/monactin (Ammonium Ionophore I, Fluka), 64 % dibutylsebacate (Selectophore, Fluka) and 33 % of PVC (Fluka). These membranes were casted on six conductive supports constituted by graphite/epoxy composites containing different percentages of graphite (from 10 to 60 % of graphite, in 10% steps) [4].

Procedures

All measurements were made under isothermal conditions. The effect of temperature on the response of the ISE's was evaluated from calibrations in the concentration range $2x10^{-5}$- $2x10^{-2}$ **M**, with ammonium chloride solutions, without adjustment of the ionic strength, at 20, 30, 40 and 50 °C. Hysteresis curves in 10^{-4} **M** ammonium chloride were plotted automatically [3] in the range from 10°C to 50°C and back again to 10°C, always in 10 °C steps.

RESULTS

Calibration at different temperatures

The results obtained in the calibrations of the ISE's at 20°C showed that the conductive support of the electrodes must contain at least 40% of graphite to provide electrodes with suitable response. The results of the calibrations of the electrodes at different temperatures are summarized in Table 1 and show that the values of the slope and E^o diminish with increasing temperature, as expected, with thermal coefficients of -0.5 mV/dec.°C for slope and -3 mV/°C for E^o, respectively. Both coefficients are independent of the content of graphite in the conductive support.

Table 1: Calibration parameters obtained at different temperatures [1]

% Graphite	T(°C)	R [2]	Slope [3] (mV/dec.)	E^o [3] (mV)
40	20	0.99995	48.7 (448.0-49.3)	181.8 (179.8-183.9)
	30	0.9999	44.1 (43.3-44.8)	158.8 (156.3-160.7)
	40	0.9998	40.1 (38.2-42.1)	126.2 (120.1-132.3)
	50	0.9997	37.5 (32.6-42.3)	105.1 (90.3-119.9)
50	20	0.99998	47.8 (47.4-48.2)	187.3 (186.0-188.5)
	30	0.9996	42.1 (41.2-42.9)	162.9 (160.2-165.7)
	40	0.99995	39.7 (37.9-41.4)	137.4 (132.0-142.8)
	50	0.9999	34.7 (33.9-35.5)	108.1 (104.3-111.9)
60	20	0.99998	48.4 (47.6-49.1)	149.6 (147.3-152.0)
	30	0.9998	44.4 (43.4-45.4)	114.3 (111.2-117.3)
	40	0.9994	40.5 (38.6-42.4)	94.4 (88.7-100.2)
	50	0.9999	32.4 (28.5-36.3)	49.4 (37.4-61.4)

1) Calculated from 6 points in the concentration range 10^{-4}- 5x10-3 M NH4Cl; 2) R is the correlation coefficient; 3) Confidence limits for a 95 % level are presented in brackets.

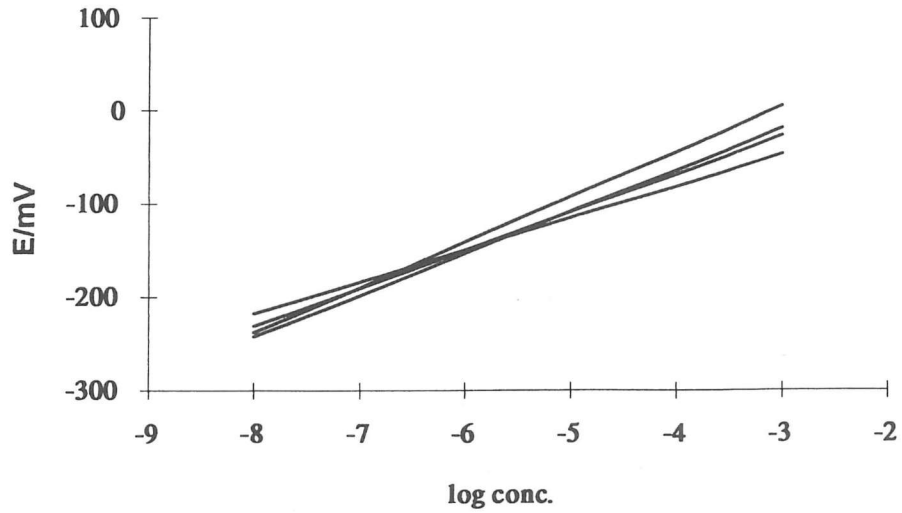

Fig. 1: Calibrations *vs.* temperature to obtain the isopotential point (electrode with 50 % of graphite)

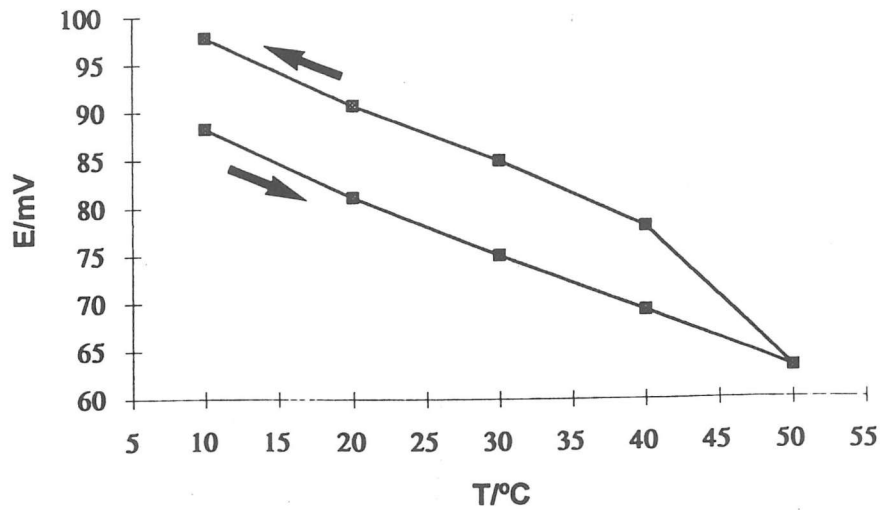

Fig. 2: Typical hysteresis curve (electrode with 50 % of graphite)

The concentration corresponding to the isopotential point falls in a range [5] around 10^{-6} **M** (as shown by a typical plot in Fig.1 for the electrode with 50% of graphite in the support) and is practically independent of the graphite content in the conductive support. This value is identical to that for an all-solid-state nitrate ISE [6] constructed with the same type of conductive support, but this is probably a coincidence without special meaning.

Hysteresis curves

The hysteresis curves obtained for the electrodes with different contents of graphite are identical (Fig.2) and show that these present little hysteresis in the 10-50ºC temperature range.

CONCLUSIONS

The effect of temperature on the response of the electrodes in the range 10 to 50oC is independent of the graphite content in the conductive support, provided this contains at least 40% of graphite to ensure that units with adequate response characteristics are obtained. The concentration of the isopotential point of the electrodes, which falls in a range around 10-6 M, also shows no variation with the percentage of graphite. In conclusion, the present results exclude the percentage of graphite in the epoxy support from the constructive parameters that influence the response characteristics of electrodes with conductive supports made of graphite/epoxy composites.

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