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EFFECT OF THE TEMPERATURE ON THE RESPONSE CHARACTERISTICS OF "ALL SOLID STATE" ISES BASED ON MERCURY SALTS APPLIED TO ELECTRICALLY CONDUCTIVE SUPPORTS*

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ABSTRACT

A study of temperature effects on the response of ISEs made with membranes constituted by HgS/Hg₂Cl₂ applied to electrically conductive epoxy supports of several types is reported. Results for operational temperature ranges, slope and standard potential variations with temperature, isopotential points, stabilization times and hysteresis curves have been obtained. These results confirm that the equilibria reached by membranes with this sensor are thermodynamically metastable, which explains why the operation of these electrodes is more troublesome than for AgCl/Ag₂S electrodes. It is shown that the decrease in the lower limit of linear response obtained by cooling the electrodes below room temperature is very limited.

KEYWORDS

Chloride-selective electrode; mercury salts; conductive epoxy-based ion-selective electrodes; temperature effects; slope coefficient; potential coefficient; isopotential point; hysteresis curves.

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INTRODUCTION

Chloride ion-selective electrodes (ISEs) with crystalline membranes constituted by mixtures of mercury(II) sulphide and mercury(I) dichloride have lower detection limits than electrodes made from silver(I) sulphide and silver(I) chloride (*p.ex.* ¹⁻³, for more complete list of references, see ³). This feature makes their use very convenient for the determination of low levels of chloride in water (*p.ex.* ^{2,4,5}) although they have troublesome operation ^{3,6,7} (see more references in ³). MARSHALL and MIDGLEY ^{2,5} suggested the use of electrodes with this type of sensor below room temperature to suppress the solubility of the mercury(I) dichloride and extend the range of chloride measurement in high-purity waters. However, they have not reported any systematic study of temperature effects on the response of the electrodes, and the cooling had apparently a limited success (shifts of potential ², longer response times ² and no improvement of the precision ⁵ at lower temperatures were observed). In previous work in this Department ³, an electrode with the same sensor mixture applied to an electrically conductive (silver loaded) epoxy support was evaluated at room temperature. It was shown that metastable equilibria occur in the sensor system, because disproportionation of mercury(I) ion to mercury(II) and mercury(0) in the membrane is thermodynamically spontaneous, and suggested that these equilibria could explain the troublesome operation of electrodes with this type of sensor.

This set of information prompted us to include electrodes with sensor constituted by a mixture of mercury(II) sulphide and mercury(I) dichloride in a systematic study of the effects of the temperature on the response of ISEs now in progress in this Department ⁸⁻¹⁰. This paper reports results obtained for electrodes with the sensor mixture applied to commercial silver loaded conductive epoxy ³ or to graphite loaded conductive epoxy, or dispersed in non-conductive epoxy, as well as for an electrode prepared by application of the mixture to a commercial hydrofobized graphite body (Ruzicka Selectrode) ^{2,5}, used for comparison purposes (for sake of brevity, these four types of electrodes will henceforth be called "silver epoxy", "graphite epoxy", "heterogeneous membrane" and "graphite body" electrodes respectively). The study covered the temperature range 10-60°C

and included calibrations at different temperatures (for determination of operational temperature ranges, slope and standard potential variations and isopotential points), stabilization times at different temperatures and hysteresis curves. Different types of conductive epoxies and heterogeneous membranes with sensor dispersed in non-conductive epoxy were used because the study ⁸⁻¹⁰ includes an investigation of the influence of the support nature on the properties of the electrodes.

EXPERIMENTAL

Equipment

Potentials were measured as in previous work ⁸ (and references therein). Readings were taken successively for six electrodes immersed in the same cell by using an electrode switch.

Constant temperature measurements were made at 10.0, 20.0, 30.0, 40.0, 50.0 and 60.0 ± 0.2 °C. The equipment for temperature control was described before ⁸.

Reagents

All chemicals were of analytical-reagent grade and were used without further purification. De-ionised water with specific resistivity > 4 MΩ cm⁻¹ was used. Further details about the preparation of solutions were given elsewhere ^{3,7}.

Preparation of the electrodes

The sensor mixture was prepared as described before ³.

The technique for construction of electrodes was described before (*p.ex.* ³ and references therein). Electrodes with four types of membrane or sensor support were prepared: sensor applied to silver loaded commercial epoxy (Epoxy Technology Inc, EPOTEK 410) ^{3,8}; sensor applied to a dispersion of graphite powder (< 50 μm, Merck, 4206) in non-conductive commercial epoxy (Ciba-Geigy, ARALDITE M with hardener HR) ^{11,12}; heterogeneous membrane, with sensor dispersed in non-conductive commercial epoxy ¹³ applied to a support of graphite loaded non-conductive epoxy support; sensor applied to a hydrofobized graphite body (Ruzicka Selectrode, Radiometer Model F3012) ^{2,5}.

For the preparation of supports made of graphite powder dispersed in non-conductive epoxy, the substances were mixed in a 1:1 weight proportion. For the preparation of heterogeneous membranes, the sensor and the epoxy were mixed in a 5:1 proportion.

Experiments

Standard techniques described before⁸ were used for evaluating the response characteristics of prepared electrodes at different temperatures. Before measurements, these were polished and conditioned as before³. All electrodes (including the reference electrode) were immersed in the work cell (measurements of the so called "isothermal type"¹⁴). Hysteresis tests to the reference electrode were described before⁸. All measurements were performed in solutions with ionic strength adjusted to 0.1 M with KNO_3 .

Hysteresis curves (of the so called "equilibrium hysteresis" type⁸) were obtained in experiments in which potential was read after thermal equilibrium and potential stabilization (≤ 0.1 mV within 5 min) at each temperature. Curves for primary ion-concentration of 10^{-3} , 10^{-2} and 10^{-1} M were obtained.

RESULTS AND DISCUSSION

Calibrations at different temperatures

For each electrode, calibrations by the standard addition technique (in the range from ca. $1 \cdot 10^{-5}$ up to $2 \cdot 10^{-2}$ M) were repeated four times at each temperature. Values of slope and standard potentials were calculated from the linear range of response for each calibration, which narrowed with the increase of temperature. Average values of the calibration parameters are presented in Table 1 (the correlation coefficients, R, of the least-squares adjustments were always > 0.999).

Values of the lower limit of linear response of the electrodes obtained from the calibration curves at the different temperatures are reported in Fig.1. They were practically independent of the type of preparation, between ca. $1 \cdot 10^{-3}$ M (at 60°C) and $1.5 \cdot 10^{-4}$ M (at 10°C). In Fig.1, values of the lower limit of linear response at different temperatures of all-solid-state chloride selective electrodes with sensor made of silver salts and applied to a silver loaded epoxy support, determined by a similar procedure⁸⁻¹⁰, are also presented. A comparison of the curves shows that the difference between the values for the two types of sensors decreases when the temperature increases. Moreover, the curves show that, in both cases, the decreases in the lower limit of linear response achieved upon cooling from 20°C to 10°C are neglectable.

Table 1

Slope (S, mV/dec) and standard potential (E^0 , mV)* values at various temperatures**

Temp.(°C)		Electrode type				Theoretical value
		Silver epoxy	Graphite epoxy	Heterogenous membrane	Graphite body	
10	E^0	37.6(3.8)	66.1(4.5)	33.5(6.2)	35.4(10.4)	-56.2
	S	-57.6(0.1)	-49.4(1.3)	-58.8(2.0)	-57.1(3.0)	
20	E^0	55.0(2.1)	64.3(4.4)	49.3(2.6)	37.1(0.3)	-58.2
	S	-54.1(1.6)	-50.5(0.3)	-54.4(1.6)	-55.3(1.2)	
30	E^0	52.5(0.6)	73.5(2.1)	44.2(0.9)	***	-60.1
	S	-56.1(0.3)	-49.2(0.5)	-58.1(0.1)	***	
40	E^0	33.3(1.9)	48.4(1.1)	47.7(1.2)	33.4(1.6)	-62.1
	S	-62.9(0.9)	-57.9(0.8)	-58.8(0.9)	-64.8(1.6)	
50	E^0	47.2(1.3)	48.2(1.6)	75.1(5.0)	42.2(1.2)	-64.1
	S	-59.5(0.8)	-58.4(0.6)	-45.7(1.6)	-62.5(0.3)	
60	E^0	45.9(3.4)	43.5(3.3)	92.5(10.0)	40.7(1.8)	-66.1
	S	-61.5(1.2)	-61.6(1.3)	-32.7(8.4)	-65.0(0.3)	

*) Against the reference electrode

** Standard deviations in parentheses

*** Not measured at 30°C

Although, in most cases, the slope values of the different types of electrodes (Table 1) were not far from the theoretical values, at different temperatures they showed erratic behaviour, specially at temperatures higher than 40°C and for the "heterogenous membrane" electrode (whose slope decreases markedly with the temperature above 40°C).

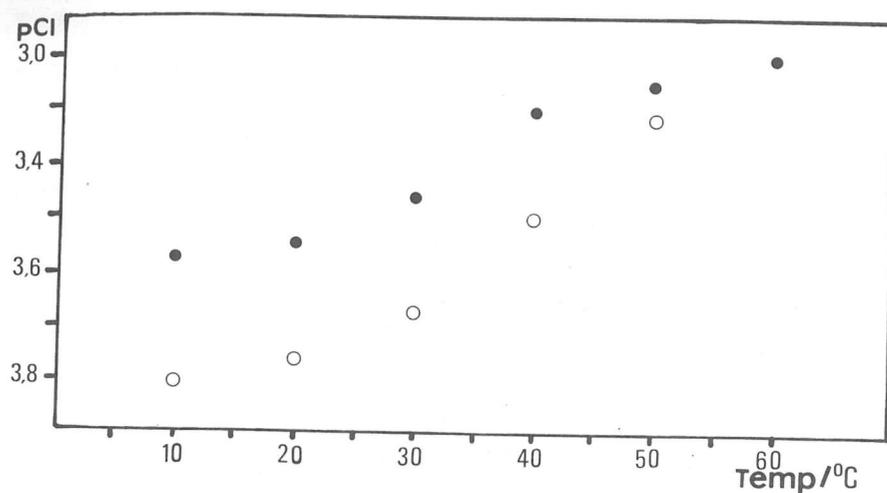


Fig.1 - Temperature dependence of the lower limits of linear response for electrodes with sensor made of: (●) silver salts; (○) mercury salts

From the slopes at different temperatures (with the mentioned restrictions about operational ranges), values of isothermal slope coefficients were calculated (Table 2). With the exception of "graphite epoxy" electrode, the electrodes showed isothermal slopes coefficients near the theoretical value ($-0.20 \text{ mV } ^\circ\text{C}^{-1}$), but values of the correlation coefficients (R) were rather low, in consequence of the erratic temperature behaviour of the electrodes.

Values at 20°C of the standard potentials of all epoxy electrodes, when corrected to express the Ag/ClAg reference electrode potential against N.H.E. (+222 mV) and to allow to the 0.1 M ionic strength (-7 mV), were found to fall in the range 264-279 mV. This is close to +268 mV, the standard potential of $\text{Hg}_2\text{Cl}_2\text{-Hg}$ system¹⁴, suggesting that there is

Table 2
Isothermal slope (mV /dec K) and standard potential (mV/K) coefficients

	Electrode type			
	Silver epoxy	Graphite epoxy	Heterogenous membrane	Graphite body
Slope coefficient *				
Temp. range (°C)	20-60	10-60	20-40	10-60
Value	-0.18	-0.27	-0.22	-0.18
R **	0.81	0.92	0.93	0.87
Potential coefficient				
Temp. range (°C)	20-60	10-60	20-60	10-60
Value	-0.24	-0.53	1.07	0.11
R **	0.44	0.82	0.91	0.60

*) Theoretical value: $-0.1984 \text{ mV /dec K}$

**) R, correlation coefficient of the least-squares adjustment

mercury(0) in the membrane to fix a_{Hg} at 1 (ref. ³ and references therein).

Plots of E° vs. T obtained from calibrations at different temperatures, showed poor linear correlation (low R values) with temperature even when the 10°C points were excluded (Table 2), which is due to the large relative dispersion of E° values and their small variation with temperature, as in other cases reported in a previous study⁸.

In conclusion, results of calibrations at successively increasing temperatures showed that operational temperature ranges were different for the four types of electrodes. "Silver epoxy" and "graphite body" electrodes showed operational temperature ranges of 10-60°C while "heterogenous membrane" and "graphite epoxy" had their temperature

ranges limited to ca. 20-40°C. These results are in agreement with potential vs. time curves at different temperatures and hysteresis curves to be discussed in the following sections

Stabilization curves

Stabilization (potential vs. time) curves at different temperatures, in 10^{-3} M chloride solutions, were obtained to assess stabilization times, and are exemplified in Fig. 2. This includes curves for the "silver epoxy" electrode (curves for the "graphite body" electrode were similar) as well as for an electrode with poor quality of response ("heterogenous membrane" electrode).

For all cases, stabilization times were shorter in the range 20-40°C. Outside this range, potential fluctuations and, or, drifts were specially marked when curves for different temperatures do not follow the sequence expected from behaviour defined by a Nernst-type equation, as shown in Fig. 2.b.

From potential readings upon stabilization, potential vs. temperature plots were obtained to determine dE/dT values used in the calculation of isopotential concentrations (see below). These plots are also included in Fig. 2.

Hysteresis curves

As discussed in previous work⁸, hysteresis experiments can be made by two procedures, "equilibrium hysteresis" and "quick hysteresis". Equilibrium hysteresis experiments (as made in the present work) are expected to be more representative because their results refer to metaestable equilibrium states in which thermal equilibrium has been reached. Their difference to expected values for equilibrium states is a measure of the extent of electrochemical disequilibrium.

In Fig. 3, equilibrium hysteresis curves (10 → 60 → 10°C and 60 → 10 → 60°C cycles) in 10^{-3} M chloride solutions are exemplified for different types of electrodes. As shown, the extent of the hysteresis was found to depend markedly on the type of the electrode, being minimum for the "graphite body" electrode (see Fig. 4 discussed below) and maximum for

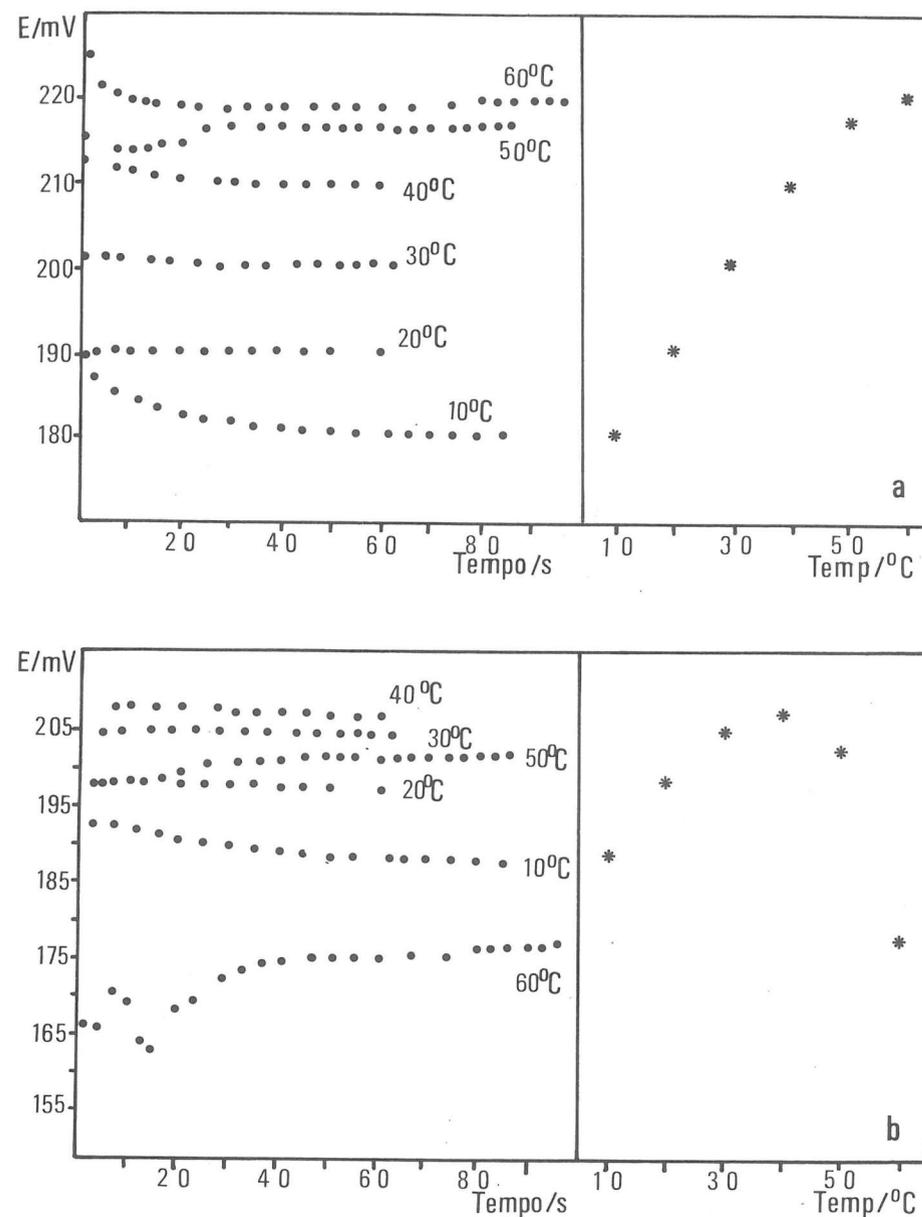


Fig. 2 - Stabilization curves (left) and correspondent potential vs. temperature curves (right) for (a) "silver epoxy" and (b) "heterogenous membrane" electrodes

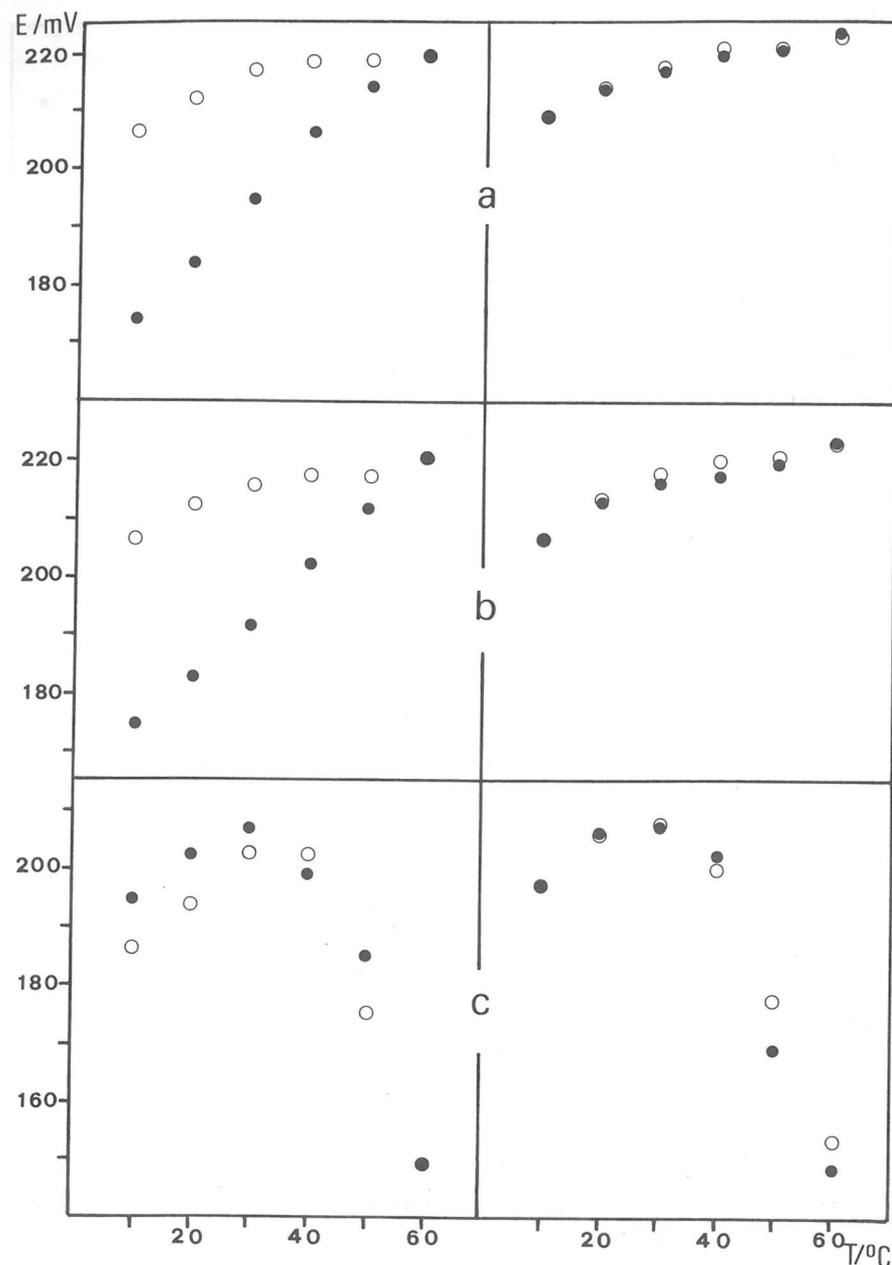


Fig. 3 - Hysteresis curves in 10^{-3} M chloride solutions for (a) "silver epoxy"; (b) "graphite epoxy"; and (c) "heterogenous membrane" electrodes. Left: 10- \rightarrow 60- \rightarrow 10°C; right: 60- \rightarrow 10- \rightarrow 60°C. (●) Heating; (○) cooling.

"graphite epoxy" and "silver epoxy" electrodes. Curves for "heterogenous membrane" electrodes showed a "break point" between 30-40°C, but they did not present very pronounced hysteresis. It is interesting to note that this shape of hysteresis curve was found for a chloride selective electrode with sensor of silver salts applied to a silver epoxy support (Fig.3 of ref.⁸) but not for the present "silver epoxy" electrode with sensor of mercury salts.

The results also showed that hysteresis curves for all the electrodes studied depend markedly on the direction of temperature variation, being more pronounced for 10 \rightarrow 60 \rightarrow 10°C cycles than for 60 \rightarrow 10 \rightarrow 60°C cycles (see Fig. 3). This observation is in agreement with other facts found in the present study, for instance, longer stabilization times and far-from-nernstian response at higher temperatures (>40°C). The behaviour is similar to the previously found in sulphide and halide all-solid-state selective electrodes with silver salts as sensors⁸, which confirms that, for electrode hysteresis, heating is more important than cooling.

As data in the literature on the influence of the concentration on the hysteresis curves are scarce^{9,15}, in the present work these were obtained at three values of the chloride ion concentrations, 10^{-1} , 10^{-2} and 10^{-3} M. In Fig. 4, hysteresis curves at these concentrations for the "graphite body" electrode are presented. The figure shows that the concentration has little influence on the extent of the hysteresis and the shape of the curves. However, the rate of potential variation with the temperature depends on the concentration, as expected from the relative values of the experimental and the isopotential concentration (about 10^2 M, see Table 3). The lower is the experimental concentration, the higher is the potential vs. temperature rate. Similar results were found for the other three types of electrodes.

Isothermal isopotential concentrations

The dispersion of the values of standard potentials prevents the calculation of isopotential points from the standard potential vs. temperature plots as in previous work^{8,9}. An alternative procedure was implemented.

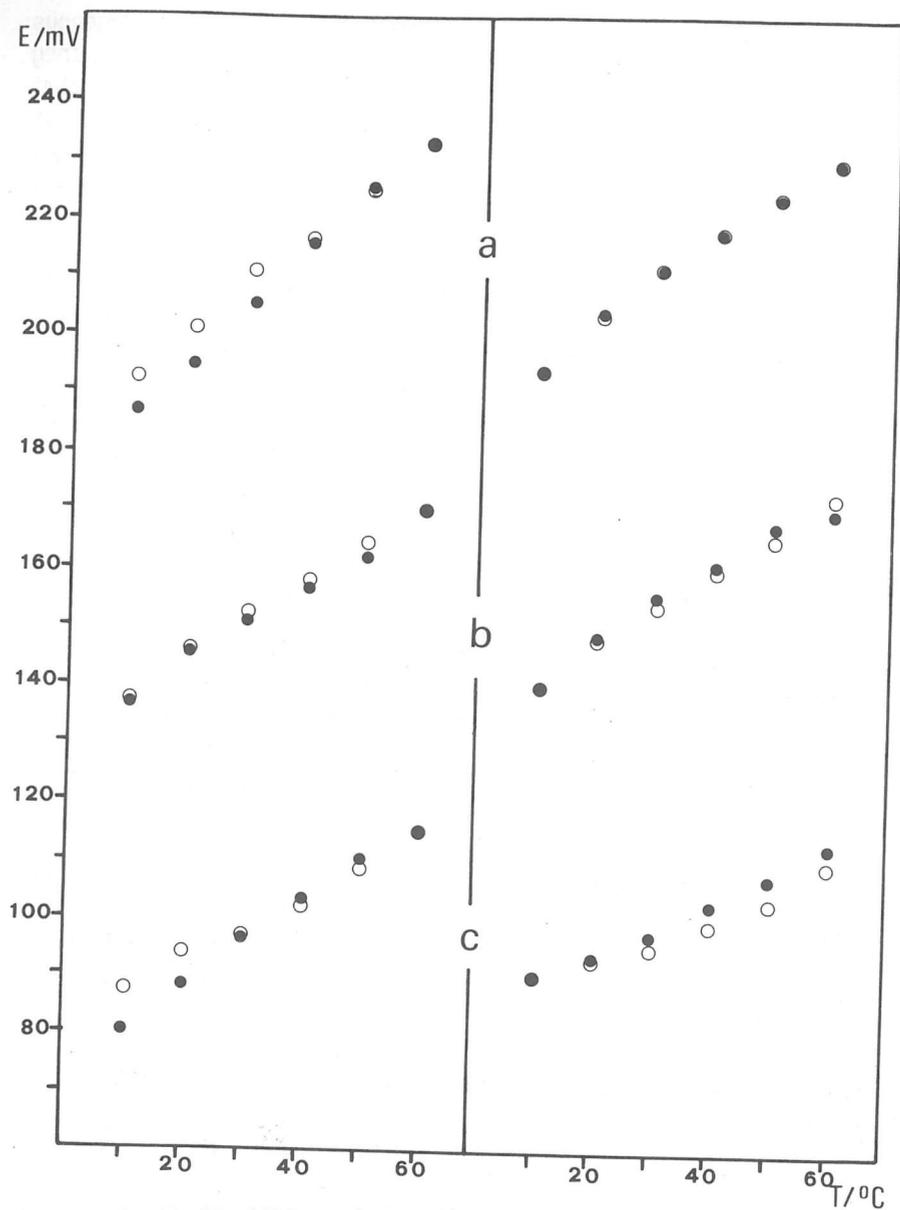


Fig. 4 - Hysteresis curves for the "graphite body" electrode in (a) 10^{-3} (b) 10^{-2} and (c) 10^{-1} M chloride solutions. Left: $10 \rightarrow 60 \rightarrow 10^\circ\text{C}$; right: $60 \rightarrow 10 \rightarrow 60^\circ\text{C}$. (●) Heating; (○) cooling.

From the response of the electrodes upon stabilization at the different temperatures in 10^{-3} M potassium chloride solutions ($I = 0.1$ M) (Fig. 2) values of dE/dT were obtained. Values of dE^0/dT were calculated through the equation

$$dE/dT = dE^0/dT + \ln [\gamma_{\text{Cl}^-} |\text{Cl}^-|] dS/dT + S d[\ln \gamma_{\text{Cl}^-} |\text{Cl}^-|]/dT$$

obtained by derivation of a Nernst-type equation with respect to the temperature. The value $\gamma_{\text{Cl}^-} = 0.77$ (at $I = 0.1$ M)¹⁴ was used and values of dS/dT were taken from Table 2. As the temperature variation of $\ln[\gamma_{\text{Cl}^-} |\text{Cl}^-|]$ is neglectable ($< 10^{-4} \text{K}^{-1}$)^{14,16}, the last term was neglected.

Using the definition of isopotential point ($dE/dT = 0$ at $\sigma_i = \sigma_{i,\text{iso}}$), the isopotential concentration can be calculated from

$$\ln [\gamma_{\text{Cl}^-} |\text{Cl}^-|_{i,\text{iso}}] = -(dE^0/dT)/(dS/dT).$$

The values of isopotential concentrations obtained are presented in Table 3 (the value at 25°C corresponding to nernstian behaviour¹⁴ is also included). The temperature ranges mentioned in Table 3 exclude the 60°C points because the plots of potential vs. temperature were no longer linear at this temperature. Values in Table 3 show good agreement between the calculated and theoretical values for "silver epoxy" or "graphite body" electrodes but a large difference for "graphite epoxy" and "heterogenous membrane" electrodes.

The values of isopotential concentrations found for "silver epoxy" or "graphite body" electrodes are similar to those previously found for similar electrodes with sensor made of silver salts⁸.

CONCLUSIONS

The results in the present work confirm the conclusion⁸ that the nature of the support and of the support-sensor internal contact influences the response characteristics of the electrodes, in particular their temperature behaviour.

Table 3
Isothermal isopotential point concentrations

Electrode type	Temp. (°C)	Concentration (M)
Silver epoxy	20-50	$1.4 \cdot 10^2$
Graphite epoxy	10-50	$3.0 \cdot 10^0$
Heterogenous membrane	20-40	$6.9 \cdot 10^0$
Graphite body	10-50	$3.6 \cdot 10^2$
Theoretical value	25	$2.4 \cdot 10^2$

The erratic temperature behaviour of the chloride selective electrodes reported in the present study confirms that the sensor constituted by mercury(II) sulphide and mercury(I) dichloride involves complex reactions and that equilibria reached are metastable³.

With reference to the relative performance of the different types of electrodes, the determination of the different characteristics showed that the quality of the response of "heterogenous membrane" and "graphite epoxy" electrodes is markedly worse than for "silver epoxy" or "graphite body" electrodes. These two electrode types present responses more close to the nernstian type in an wider temperature range. Of the two, the "graphite body" electrode showed less pronounced hysteresis and so this electrode preparation technique^{2,5} seems to be particularly suitable for the implementation of the chloride electrode with sensor constituted by mercury(II) sulphide and mercury(I) dichloride. However, as this was not observed for other types of sensors⁸, this is not a general conclusion.

When the chloride selective electrodes with sensors based in mercury salts or in silver salts are compared, the difference in the lower limits of linear response, as obtained from the calibrations in the present work,

decreases when the temperature increases. In consequence, the advantage of the use of the mercury salts electrode for measurements at low chloride concentrations is lost at higher temperatures. On the other hand, it was found that, in practice, cooling below room temperature brings no appreciable widening of the linear range of response of these electrodes.

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