

Performance Characteristics of Cells Containing Two Potentiometric Sensors: Application to a Cell Containing Hydralazinium and Chloride Electrodes

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Abstract

Conventional plastic membrane electrode, selective to hydralazinium cation (Hz) was constructed by incorporation of Hz-phosphotungstate ion associate in a poly(vinyl chloride) membrane. The influence of membrane composition, pH of the test solution and foreign ions on the cell performance was investigated. This was compared to the corresponding influence on a cell constructed by replacing the reference electrode in the conventional cell with Cl-selective electrode. The results indicated that the first cell showed Nernstian behavior, while the latter exhibited super Nernstian response. The selectivity for both cases was high. However the working pH range was narrower in case of the cell with two sensors.

Keywords: Hydralazinium-electrode, Phosphotungstate, Super Nernstian slope, Hydralazine hydrochloride, Plastic membranes

1. Introduction

Hydralazine hydrochloride (hydralazinium chloride, HzCl) is an important pharmaceutical compound used as a vasodilator in the treatment of hypertension (Ellershaw and Gurney 2001; Li et al., 2010). In a previous work a Hz-selective membrane electrode was prepared by incorporation of Hz-tetraphenylborate ion-pair into a poly(vinyl chloride) (PVC) matrix (Badawy et al., 1988). Although the electrode exhibited good performance characteristics, its life span was only about 2 hours. This created the demand to investigate the use of other ion-associates that are more lipophilic than Hz-tetraphenylborate, as ion-exchanger for the construction of plastic membrane Hz-electrodes of longer life times. This was done by introducing hydralazinium phosphotungstate (Hz₃PT) ion associate as the ion-exchanger (Shoukry et al. 2006). The electrode showed Nernstian behavior over a life span of 17 days.

It was reported that one of the main disadvantages of direct potentiometry is the relatively high percent of error associated with slight indeterminate deviation of the reading (Christian 2004). Thus, for electrodes responsive to mono-, di-, and tri-valent ions; only 1.0 mV deviation results in a 12.0, 8.0 and 4.0 % error in the final determination, respectively. These error percentages were calculated assuming Nernstian behavior of the electrode. This drawback restricted the application of the traditional potentiometric technique using ion-selective electrodes especially for ions with high valency. However, the error can be, significantly decreased if the signal to noise ratio increased by increasing the graph slope.

In the present paper, a new technique has been applied successfully by which calibration graph of multiple Nernstian slope, and consequently higher signal to noise ratio, is obtained. The new technique depends on employing cells containing two ion selective electrodes, one for Hz⁻ and the other, in place of the reference, for the counter ion, Cl⁻. The latter was a polycrystalline silver chloride-based electrode (Hodrejarve 1985). The cell potential in this case is given by:

$$E_{\text{cell}} = E_{\text{Hz}} - E_{\text{Cl}} \quad (1)$$

$$E_{\text{cell}} = [E^{\circ}_{\text{Hz}} + 2.303 \text{ RT/F} (\log a_{\text{Hz}})] - [E^{\circ}_{\text{Cl}} - 2.303 \text{ RT/F} (\log a_{\text{Cl}})] \quad (2)$$

where E° , R, T, F and (a) have their familiar meanings.

For a dilute solution of HzCl, $a_{\text{Hz}} = a_{\text{Cl}}$,

$$E_{\text{cell}} = (E^{\circ}_{\text{Hz}} - E^{\circ}_{\text{Cl}}) + 2.303 \text{ RT/F} (\log a_{\text{Hz}}) + 2.303 \text{ RT/F} (\log a_{\text{Cl}}) \quad (3)$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} + 2 (2.303 \text{ RT/F}) (\log a_{\text{Hz}}) \quad (4)$$

Equation (4) shows that on plotting E_{cell} versus $\log a_{\text{Hz}}$, a straight line of double Nernstian slope is obtained, providing that the two sensors are functioning in a thermodynamic manner.

In a previous study (Shoukry, 1988) a cell containing two indicator electrodes was used for potentiometric titration of hexadecylpyridinium bromide with standard solution of sodium tetraphenylborate. Titration curves with sharp peaks or troughs, at the equivalence points, were obtained. Nevertheless, the study didn't include characterization of the cell's performance.

In the present work, the performance characteristics of cells containing two indicator electrodes are studied. Calibration graph's slope, stability and life span of the constructed cells as well as their responses towards changes of pH and presence of foreign ions have been investigated.

2. Experimental

2.1 Reagents and Materials

All chemicals used were of analytical grade. Bi-distilled water was used throughout all experiments. The Hz-PT ion-associate was prepared by a method similar to that described before by Shoukry et al. (1988). The composition of the produced ion-associate was determined by elemental analysis using Elementar Microcube. The agreement between calculated and found values was confirming the stoichiometry of (3:1) (Hz:PT).

2.2 Construction of Electrodes

2.2.1 The chloride-selective electrode

A silver rod of 10.0 cm length and 5.00 mm diameter was tightly insulated by polyethylene tube leaving 1.0 cm at one end for coating and 0.5 cm at the other end for connection. The 1.0 cm terminal was electrolytically coated with AgCl. The coating was carried out in an 0.1 M NaCl solution with the silver rod as the anode and a platinum electrode of 1.0 cm² surface area as the cathode. The coating time was 10 minutes with current density of about 10 mA/cm². The prepared electrode was preconditioned before use by soaking in a 10⁻² M NaCl solution for 30 minutes.

2.2.2 The plastic membrane Hz-selective electrode₂

In about 5 mL tetrahydrofuran, 5.0, 10.0 or 15.5 mg of the ion-exchanger (Hz-PT) were dissolved and as well as 120 mg of each of PVC and dioctylphthalate (DOP), as plasticizer and solvent mediator. The produced solution mixture was poured into a 7.5 cm diameter Petri dish and left to dry in air. The obtained membrane was used to prepare the electrodes as previously described by Issa et al. (1999); the internal solution of the electrode was 10⁻³ M in HzCl and 10⁻¹ M in NaCl.

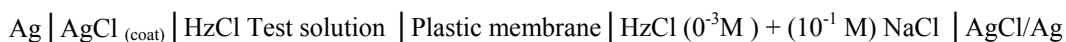
2.3 Potentiometric Studies and Electrochemical Systems

Potentiometric measurements were carried out with an Orion, Model 420A pH/mV meter. A Caron circulator thermostat was used to control the temperature of the test solution. The following electrochemical systems were employed:

2.3.1 System containing one ion-selective electrode

Ag | AgCl_(ref) | HzCl Test solution | Plastic membrane | (10⁻³M) HzCl, (10⁻¹ M) NaCl | AgCl | Ag

2.3.2 System containing two ion-selective electrodes



2.4 Construction of the Calibration Graphs

Suitable increments of standard HzCl solution were added to 50 mL of 10^{-6} M HzCl solution to cover the concentration range of 10^{-6} M to 1.7×10^{-2} M. In this solution the sensor and the reference electrode or the two sensors were immersed and the emf was recorded after 10 s, at 25°C , for each addition.

2.5 Selectivity

The selectivity coefficients of the Hz- selective electrode, ($K^{\text{pot}}_{\text{Hz,j}}$) or that of the cell containing Hz- and Cl- electrodes, ($K^{\text{pot}}_{\text{Hz,j}} k^{\text{pot}}_{\text{Cl,x}}$) towards different cationic species j^{z+} and different salts $j_n^{z+} x_m^{y-}$ ($nz = my$), respectively, were determined by the separate solution method (SSM) (Cosofret and Buck 1984) and matched potential method (MPM) (Ganjali et al. 2010).

3. Results and Discussion

3.1 Composition of membrane

Three membrane compositions were tried, in a previous work (Shoukry et al., 2006), as given in Table 1. The best responses over a relatively wide range of HzCl concentration are exhibited by electrodes made by using membranes containing 2.1 % ion associate. The response time was always < 10 s. However, membranes containing 4.0% ion-pair exhibited more stable readings, for this reason, electrodes made by using membranes of this composition (4%) were selected for carrying out all consequent studies.

3.2 Response characteristics of cell containing Hz- and reference electrodes

The performance characteristics of Hz-selective electrodes were investigated as a function of soaking time. For this purpose the electrode was soaked in 10^{-3} M solution of HzCl and the calibration graphs (pHz vs E, mV) were plotted after different time intervals in a period of 17 days. The electrode proved reasonable activity throughout this period. The conditioning time required for activating the phase boundary exchange process at the surfaces of the membranes was 30 minutes with concentration range of $1.58 \times 10^{-5} - 1.7 \times 10^{-2}$ M HzCl (Fig. 1a). On soaking the electrode for longer than 17 days, the calibration graph slope decreased gradually. This decrease in the response of the electrode is most probably due to leaching of the active ingredients from the gel layer at the membrane surface to the bathing solution and/or to appearance of asymmetry potential arises as a result of surface deformation. The results also reveal that the origin of plastic membrane electrode potential is phase-equilibrium at the interfacial junction separating the hydrated gel layer from the test solution (Pungor 2001) rather than an equilibrium associated with ionic transport through the membrane body (Morf 2001).

3.3 Response characteristics of cell containing two ion selective electrodes

The cell produced calibration graphs of slopes of almost double Nernstian value. The cell attained stable potential within less than 10 seconds when the concentration of HzCl changed. The graphs were obtained at different intervals of soaking the electrodes in 10^{-3} M HzCl (Figure 1b). From this figure, it is evident that only 30 minutes of soaking is sufficient, as conditioning time, for the activation of the cell where a calibration graph of average slope of 107.16 mV/ concentration decade was obtained. The cell retained this slope over fourteen days of continuous soaking, after which a gradual decrease in the slope value was observed. Therefore, it is recommended to store the electrodes in a closed vessel in a refrigerator while not in use.

3.4 Effect of pH

The effect of pH of the HzCl test solution on the potential reading is graphically represented in Figure 2. The pH of the initial solution is altered by the addition of small volumes of HCl and /or NaOH (0.1 – 1.0 M each). For cell containing Hz-selective electrode and reference electrode (Fig. 2 a), the pH has negligible effect within a wide range of pH-values extending from 3.2 – 9.4. In this range the electrode can be safely used for Hz determination without interference of Hydronium or hydroxyl ions. On the other hand, for cell containing Hz and Cl-sensors (Fig. 2 b), the working pH range of the cell was much narrower (4.2 – 6.0). This may be attributed to the fact that the pH-change affects two working electrodes surfaces instead of one as in case of the traditional cell. From Fig. 2b, it is clear that at pH-values higher than 6.0, the cell potential increases gradually. This may be attributed to interference of the hydroxyl ions with chloride ions at the surface of the AgCl-indicator electrode. This is confirmed by the fact that the cell potential change within this pH-range was found to be reversible. This excludes the possibility of passivation of the AgCl-electrode surface as a result of irreversible surface adsorption.

3.5 Selectivity

3.5.1 Cell containing Hz- and reference electrodes

The selectivity of the Hz-responsive electrodes was studied by applying the separate solution (Cosofret and Buck, 1984) and the matched potential (Ganjali et al., 2010) methods as previously described. The selectivity coefficients towards Na^+ , K^+ , Mg^{2+} and Cd^{2+} , as obtained by the separate solution method were 4.2×10^{-3} , 5.8×10^{-3} , 1.7×10^{-3} and 9.20×10^{-3} , respectively. In case of applying the matched potential method, the corresponding values were 5.00×10^{-2} , 5.3×10^{-2} , 2.4×10^{-2} and 3.30×10^{-2} , respectively. It is noticeable that the values obtained by the matched potential method are, in general higher than those obtained by the separate solution method, this may be attributed to the non-Nernstian behavior of the interfering ion in case of the separate solution method. However, the results, as obtained by the two methods, revealed high selectivity of the electrodes for Hz towards different cationic species.

3.5.2 Cell containing Hz- and Cl- selective electrodes

3.5.2.1 Application of the separate solution method

The cell potential is measured for two separate solutions, one containing HzCl of activity $a_{\text{Hz}} = a_{\text{Cl}} = 10^{-3} \text{ M}$, E_1 , and the other containing the interferent salt $\text{J}_m^{z+} \text{X}_n^{y-}$, where $mz = ny$, and the activity $a_j = (m/n) a_x$, E_2 .

$$E_1 = [E^\circ_{\text{Hz}} + (2.3RT/F) \log a_{\text{Hz}}] - [E^\circ_{\text{Cl}} - (2.3RT/F) \log a_{\text{Cl}}] \quad (5)$$

where E° , R , T , F and (a) have their familiar meaning.

$$E_1 = K + (2.3RT/F) \log a_{\text{Hz}} a_{\text{Cl}} \quad (6)$$

where $K = E^\circ_{\text{Hz}} - E^\circ_{\text{Cl}}$

E_2 is given by Nicolsky (1937) equation,

$$E_2 = [E^\circ_{\text{Hz}} + (2.3RT/F) \log k^{\text{pot}}_{\text{Hz,J}} (a_j)^{m/z}] - [E^\circ_{\text{Cl}} - (2.3RT/F) \log k^{\text{pot}}_{\text{Cl,X}} (a_x)^{n/y}] \quad (7)$$

$$E_2 = K + (2.3RT/F) \log k^{\text{pot}}_{\text{Hz,J}} + (2.3RT/F) \log (a_j)^{m/z} + (2.3RT/F) \log k^{\text{pot}}_{\text{Cl,X}} + (2.3RT/F) \log (a_x)^{n/y} \quad (8)$$

$$E_2 = K + (2.3RT/F) \log k^{\text{pot}}_{\text{Hz,J}} k^{\text{pot}}_{\text{Cl,X}} + (2.3RT/F) \log (a_j)^{m/z} (a_x)^{n/y} \quad (9)$$

From (6) and (9),

$$(2.3RT/F) \log k^{\text{pot}}_{\text{Hz,J}} k^{\text{pot}}_{\text{Cl,X}} = (E_2 - E_1) + (2.3RT/F) \log a_{\text{Hz}} a_{\text{Cl}} - (2.3RT/F) \log (a_j)^{m/z} (a_x)^{n/y} \quad (10)$$

$$\log k^{\text{pot}}_{\text{cell}} = (E_2 - E_1) / (2.3RT/F) + \log a_{\text{Hz}} a_{\text{Cl}} - \log (a_j)^{m/z} (a_x)^{n/y} \quad (11)$$

$k^{\text{pot}}_{\text{cell}}$ is the selectivity coefficient of the cell ($k^{\text{pot}}_{\text{Hz,J}} k^{\text{pot}}_{\text{Cl,X}}$).

It is noticeable that equation (11) is corresponding to the following equation which is applied for a cell containing one sensor electrode (Issa et al., 1999)

$$\log k^{\text{pot}}_{\text{Hz,J}} = (E_2 - E_1) / (2.3RT/F) + \log a_{\text{Hz}} - \log a_j^{z+} \quad (12)$$

The obtained $\log k^{\text{pot}}_{\text{cell}}$ values are given in Table (3). The results revealed high selectivity of the cell containing two sensors for HzCl towards different inorganic salts.

3.5.2.2 Application of the matched potential method.

The selectivity of the cell was measured by determining the concentration ratio of HzCl and the interfering salt $\text{J}_m^{z+} \text{X}_n^{y-}$ that causes the same potential change when added to a reference HzCl solution. Thus, the change in potential was measured upon changing HzCl concentration, then the interfering salt was added to an identical reference solution until the same potential change was obtained. The method (Ganjali, 2010) is recommended by IUPAC. It

has the advantage that it gets rid of the limitations of the other methods based on the Nicolsky-Eisenman equation (Girault, 2004, and Koryta, 1986). The main limitation is the non-Nernstian behavior of the interfering ions. According to this method, the selectivity coefficient is calculated as the selectivity ratio of the primary molecule (HzCl) and the interfering salt $J_m^{z+} X_n^{y-}$ that gives the same potential change in a reference solution,

$$k_{\text{cell}}^{\text{pot}} = \Delta C_{\text{HzCl}} / C_{J_m X_n} \quad (13)$$

where ΔC_{HzCl} and $C_{J_m X_n}$ are the change in HzCl concentration and the concentration of the interfering salt that cause the same potential change in a reference solution of HzCl.

Collective results of $k_{\text{cell}}^{\text{pot}}$ obtained for the investigated cells towards NaCl, KCl, NaNO_3 , KNO_3 , CH_3COONa , MgCl_2 , Na_2SO_4 , $\text{Cd}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$ and MgSO_4 as obtained by the separate solution and matched potential methods are given in Table (3). The results revealed that the proposed cells showed comparable selectivity coefficients by applying the two methods although the values obtained by the MPM were, in general, slightly lower than those by the SSM. It is also noteworthy that the values of $k_{\text{cell}}^{\text{pot}}$ for monovalent salts are higher than those for salts containing divalent ions, this can be explained on the base that electrostatic nature of monovalent salts in its hydrated forms is more relevant to those of a hydralazinium chloride than divalent ions-containing salts.

4. Conclusion

Potentiometric cells, containing two ion selective electrodes, one for Hz- and the second for Cl-, exhibit comparable performance characteristics to those of cells containing Hz and a reference electrode. However, these cells exhibit calibration graphs (E_{cell} versus pH_{Hz}) with slopes of about double Nernstian values.

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References

- Badawy, S.S. , Shoukry, A. F., Rizk, M.S., and Omar M.M. (1988). Hydralazine-selective PVC membrane electrode based on hydralazinium tetraphenylborate. *Talanta*, **35**(6), 487-489.
- Christian, G. D. (2004). *Analytical Chemistry*, John Wiley & Sons, Inc. 6th Edn., p. 383.
- Cosofret, V. V. and Buck, R. P. (1984). Phenothiazine drug poly (vinyl chloride) matrix membrane electrodes and their use in pharmaceutical analysis. *Analyst*, 109, 1321-1325.
- Ellershaw, D. C. & Gurney, A. M. (2001). Mechanisms of hydralazine induced vasodilation in rabbit aorta and pulmonary artery. *British Journal of Pharmacology*, 134, 621-631.
- Ganjali, M. R., Faridbod, F., Larijani, B., Riahi, S., Hosseini, M., Esfahani, E. N. & Norouzi, P. (2010). Terazosin potentiometric sensor for quantitative analysis of terazosin hydrochloride in pharmaceutical formulation based on computational study. *Int. J. Electrochem. Sci.*, 5, 200-214.
- Girault, H. H. (2004). *Analytical and physical electrochemistry*, EPFL Press, Marcel Dekker, Inc., NY 10016, USA.
- Hodrejarv, H. (1985). *Ion-selective Electrodes 4*, Ed. E. Pungor, Elsevier Science Publishers, The Netherland, p. 449.
- Issa, Y.M., Abdel-Ghani, N. T., Shoukry, A.F. and Ahmed, H. M. (1999). Amineptine plastic membrane electrode based on its ion-associate with tetraphenylborate and phosphomolybdic acid. *Mikrochimica Acta*, 132, 83-88.
- Koryta, J. (1986). Ion-selective electrodes. *Annual Review of Materials Science*. 16, 13-27.
- Li, Y., Saito, Y., Kuwahara, K., Rong, X., Kishimoto, I., Harada, M., Horiuchi, M., Murray, M. & Nakao, K. (2010). Vasodilator therapy with hydralazine induces angiotensin AT2 receptor-mediated cardiomyocyte growth in mice lacking guanylyl cyclase-A. *British Journal of Pharmacology*, 159, 1133-1142.
- Morf W. E. (1981). *The Principles of Ion-selective Electrodes and of Membrane Transport*, Akademiai Kiado, Budapest, p.115.
- Pungor, E. (2001). The new theory of ion-selective electrodes. *Sensors*, 1, 1-12.
- Shoukry, A. F. (1988). Use of two ion-selective electrode-containing cells for potentiometric titration of hexadecylpyridinium bromide. *Analyst*, 113, 1305-1308.

Shoukry, A.F., Badawy, S.S. and Farghali, R. (1988). Hexadecylpyridinium-phosphotungstate ion association in construction of a hexadecylpyridinium cation selective electrode. *Anal. Chem.*, 60, 2399-2402.

Shoukry, A.F., Marafie, H. M., El-Shatti, L. A. (2006). X-ray photoelectron spectroscopy and electron microscopy of hydralazinium ion-selective electrode membrane's surface. *Electroanalysis*, 8, 779-785.

Table 1. Effect of membrane composition on Hz-electrode performance (30 minutes soaking)

Ion pair % (mg)	DOP % (mg)	PVC % (mg)	Range M	Slope*	Response Time, sec
2.0 (5.0)	48.98 (120)	48.98 (120)	2.74×10^{-6} - 1.70×10^{-2}	56.67	< 10
4.0 (10.0)	48.00 (120)	48.00 (120)	1.58×10^{-5} - 1.70×10^{-2}	53.80	<10
6.1 (15.5)	46.97 (120)	46.98 (120)	9.33×10^{-6} - 1.70×10^{-2}	49.67	<10

* mV/Hz concentration decade

Table 2. Effect of soaking on Hz-electrode performance

Soaking time	Slope	Concentration range (M)
0.5hour	53.80	$1.58 \times 10^{-5} - 1.7 \times 10^{-2}$
1 hour	55.490	$3.16 \times 10^{-6} - 1.7 \times 10^{-2}$
2 hours	55.000	$6.31 \times 10^{-6} - 1.7 \times 10^{-2}$
24 hours	54.030	$4.00 \times 10^{-6} - 1.7 \times 10^{-2}$
48 hours	57.640	$1.26 \times 10^{-6} - 1.7 \times 10^{-2}$
72 hours	60.030	$6.31 \times 10^{-6} - 1.7 \times 10^{-2}$
8 days	63.011	$1.00 \times 10^{-6} - 1.7 \times 10^{-2}$
10 days	59.990	$6.31 \times 10^{-6} - 1.7 \times 10^{-2}$
17 days	54.980	$6.31 \times 10^{-6} - 1.7 \times 10^{-2}$

* mV/Hz concentration decade

Table 3. Selectivity coefficients, $K_{Hz,j} K_{Cl,x}$, of a cell containing Hz and Cl⁻ selective electrodes, for HzCl towards inorganic salts, at 25°C

Interferent	SSM*	MPM**
NaCl	1.90×10^{-1}	8.30×10^{-3}
KCl	2.40×10^{-1}	9.79×10^{-3}
NaNO ₃	1.20×10^{-2}	2.08×10^{-3}
KNO ₃	1.23×10^{-2}	4.59×10^{-3}
CH ₃ COONa	1.10×10^{-2}	3.95×10^{-3}
Na ₂ SO ₄	5.86×10^{-3}	3.48×10^{-3}
MgCl ₂	1.27×10^{-1}	8.40×10^{-3}
MgSO ₄	0.37×10^{-2}	1.31×10^{-3}
Mg(NO ₃) ₂	7.46×10^{-3}	2.38×10^{-3}
Cd(NO ₃) ₂	2.23×10^{-3}	1.14×10^{-3}

*Separate solution method.

**Matched potential method

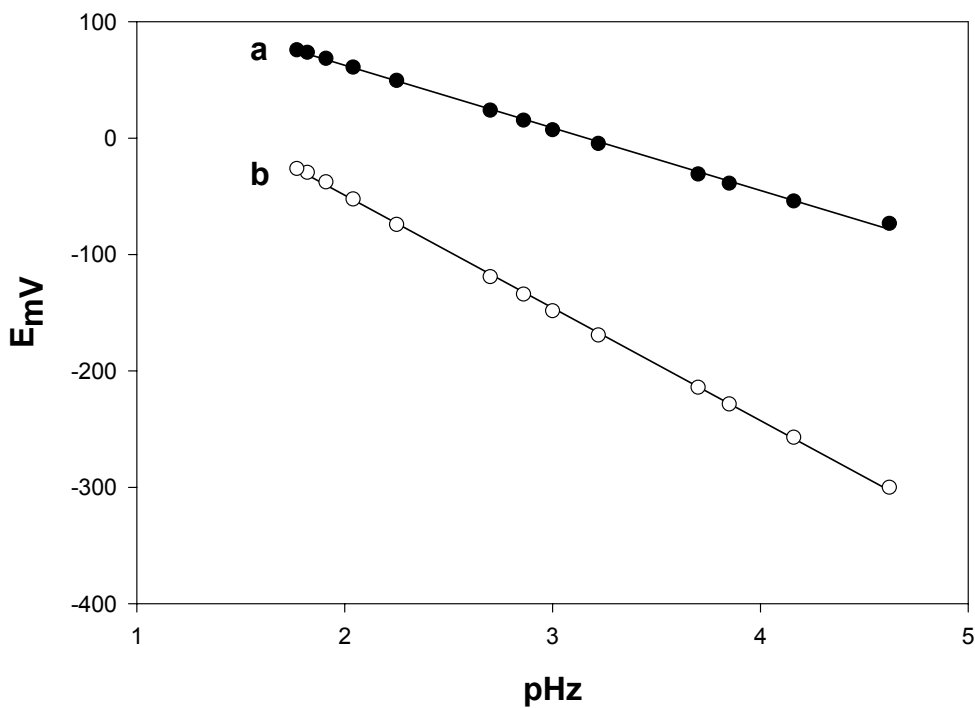


Figure 1. Calibration graphs obtained after 30 minutes conditioning time for (a) cell containing Hz- and reference electrode and (b) cell containing Hz- and Cl- selective electrodes

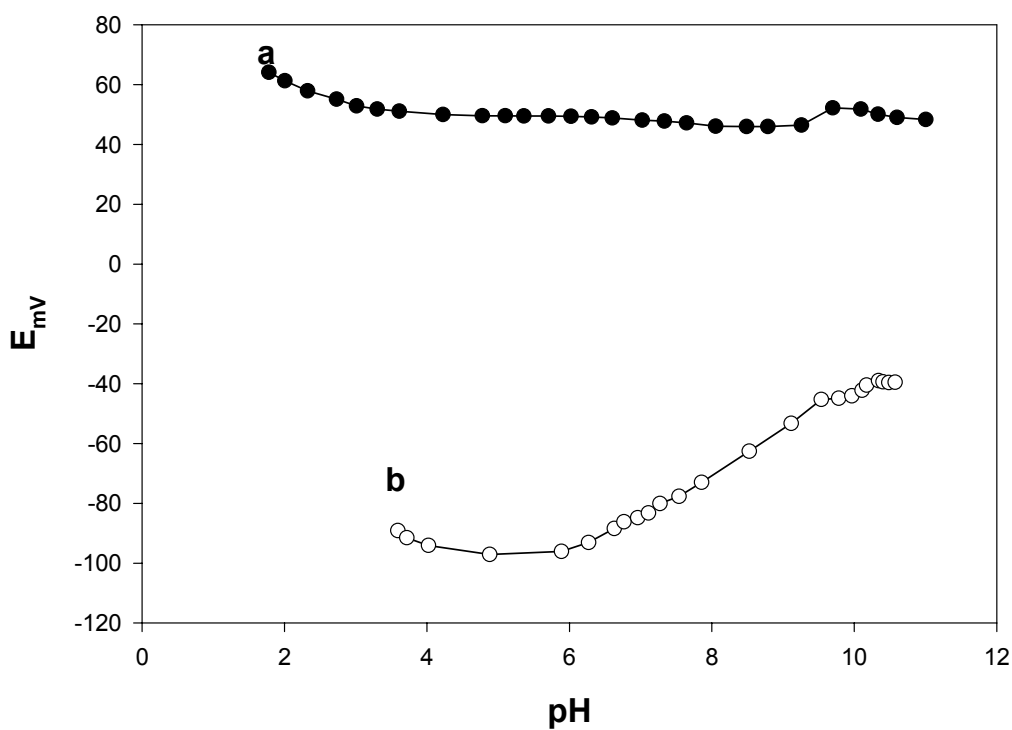


Figure 2. Effect of pH of the test solution on the potential of (a) cell containing Hz- and reference electrodes and (b) cell containing Hz- and Cl- responsive electrodes