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Comparison of the vanadyl-selective electrodes prepared by sol–gel and PVC membrane techniques

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ABSTRACT

Sol-gel and polymeric membrane electrodes, based on thiacalix[4]arene as a neutral carrier, were successfully developed for the detection of VO2+ in aqueous solutions. The sol-gel and PVC membrane electrodes exhibited linear response with Nernstian slopes of 29.3 and 28.4 mV per decade, respectively, within the vanadyl ion concentration ranges from 1.0 × 10-6 to 1.0 × 10-1 mol dm-3 and from 1.0 × 10-5 to 1.0 × 10-1 mol dm-3 for sol-gel and PVC membrane sensors. The PVC-based and sol-gel electrodes show detection limits of 3.1 × 10-6 and 4.9 × 10-7 mol dm-3, respectively, and also response time of about 15 s to achieve a 95% steady potential for VO2+ concentration. By testing the stability lifetimes of the electrodes over a six-month period, no significant change was observed in the performance of the sol-gel electrode, however, the PVC-based vanadyl-selective electrode exhibited a gradual decrease in the slope after two months. Investigating the influence of membrane composition, the pH of the test solution, and the interfering ions on the electrodes performance revealed good selectivity of electrodes for a number of alkali, alkaline earth, transition and heavy metal ions. The determined isothermal temperature coefficients of these electrodes showed a better thermal stability of sol-gel electrode rather than that of the PVC-based vanadyl-selective electrode, however, the electrodes performance is deteriorated by temperatures higher than 50 °C.

Keywords: Vanadyl sensor; Sol-gel process; Thiacalix[4]arene; Poly(vinyl chloride); Potentiometry.

INTRODUCTION

Vanadium which is an important element in environmental and biological studies, is essential for normal cell growth in trace amounts (ng/ml) but toxic at higher concentrations (μg/ml). The toxicity of vanadium is dependent on its oxidation state in which V (V) as vanadate is more toxic than V (IV) as vanadyl ions. Although vanadium can exist in oxidation states from II to V in aqueous solution, but most reported methods have focused on its determination in the oxidation states of IV and V as the most common forms encountered in inorganic and biological systems. Vanadium is an important constituent of steel, petroleum and alloy industries and is also used as a catalyst. In aqueous solution most of the reduced vanadium species found to exist as vanadyl (VO2+) which forms strong complexes with a great variety of ligands including proteins and also the VO2+ solutions are stable for many months in strongly acidic medium [1, 2].

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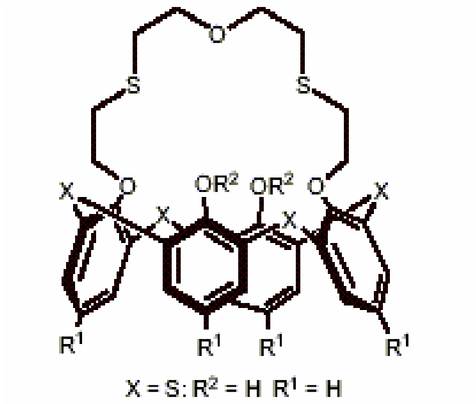
Several methods have been used to determine vanadium species including liquid chromatography coupled with spectrophotometric detection [3–6], inductively coupled plasma atomic emission spectrometric detection (ICP-AES) [7], inductively coupled plasma mass spectrometric detection (ICP-MS) [8, 9] as well as the determination of total vanadium concentration by methods with ICP-MS and catalytic determination [10–13]. On the other hand, although the potentiometric methods of analysis with ion-selective electrodes are simple, cheap and applicable to real samples but there are just a few reports on the VO2+ selective electrodes [14-16]. Hence, the development of highly sensitive and rapid methods for determination of trace amounts of vanadyl is of considerable interest.

Due to advantages of the thiacalix[4]arenas, various types of these compounds are used for the preparation of ISEs [17-22]. Scheme 1 exhibits the thiacalix[4]arene chosen by this study.



Scheme 1. Structure of thiacalix[4]arene used as ionophore.

Sol-gel technology involves the fabrication of materials through the hydrolysis and condensation of suitable alkoxysilane precursors. Composite materials based on sol-gels have been employed in electrochemical sensing devices. The driving force for these efforts is that sol-gel chemistry provides a relatively simple way to incorporate recognition species in a stable host environment [23]. On the other hand, the sol–gel route provides a useful method to prepare inorganic and organic–inorganic hybrid materials for use in chemical analysis. The inherent usefulness of this approach is mainly due to the ease at which sol–gel-based materials can be prepared, modified, and processed. The mild reaction conditions afford an opportunity to incorporate various molecules such as dyes, organic and organometallic reagents into a glass composite. This can be readily achieved by simple doping of the reagent into the sol prior to its gelation, as demonstrated by Avnir et al. [24].

In this work, vanadyl ion-selective electrodes were investigated by preparing their sensing membranes using sol–gel technique at low temperature (80 °C) and poly (vinyl chloride) (PVC). The potentiometric response properties and selectivity of electrodes were evaluated by the response potentials and selectivity coefficients. The sensors exhibit significant high sensitivity, stability, and selectivity for VO2+ ions over many common ions and are successfully used for determining VO2+ ions in spiked samples.

EXPERIMENTAL

1. Apparatus and reagents

All potentiometric measurements were made with a pH/mV meter ion analyzer in stirred solutions. In all instances, a saturated calomel electrode (SCE) was used in conjunction with the respective indicator electrode. A Haake Model FK2 circulation water bath was used to control the temperature of the test solution. A digital pH meter (Corning Model 125) was used for measuring pH. Calix[4](O3S2-crown-5)ether (TCA) was synthesized according to procedure described previously [25]. All of used reagents were at analytical reagent grade. Acetonitrile (AN), acetophenone (AP), dibuthyl phthalate (DBP), nitrobenzene (NB), potassium tetrakis(p-chlorophenyl) borate (KTPClPB), sodium tetraphenyl borate (NaTPB), oleic acid (OA), 2-nitrophenyl octyl ether (2-NPOE), dibutyl sebacate (DBS), high molecular weight poly(vinyl chloride) (PVC), tetrahydrofuran (THF), ethanol (C2H5OH), tetraethoxysilane (TEOS), diethoxydimethylsilane (DEDMS) and other reagents were obtained from Merck or Fluka chemical companies.

2. PVC membrane procedure

The general procedure used to prepare the PVC membrane was to mix thoroughly 30 mg of powdered PVC, 62 mg of plasticizer DBS and 5 mg of additive KTPClPB in 2 ml of dry freshly distilled THF. 5 mg of TCA was added to this solution and mixed very well. The resulting clear mixture was transferred into a 2 cm diameter glass dish. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (4 mm o.d.) was dipped into the mixture for about 10 s so that a nontransparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the solution and kept at room temperature for about 2 h. The tube was then filled with internal solution (1.0 × 10-3 mol dm-3 vanadyl ion + 0.185 mol dm-3 HCl + 0.20 mol dm-3 CH3COONa). These amounts of HCl and CH3COONa produce a buffer solution with pH of 3.5 in internal solution. The electrode was finally conditioned for 24 h by soaking in a 1.0 × 10-2 mol dm-3 VO2+ solution. A silver/silver chloride reference electrode was used as an internal reference electrode. The ratios of various ingredients, concentration of equilibrating solution and time of contact were optimized to provide a reproducible, noiseless and potentially stable membrane.

3. Sol–gel procedure

Polymerization and drying processes for the sol–gel membranes were performed according to previously reported details [26]. TEOS (90 µL), DEDMS (250 µL), ethanol (280 µL), 0.1 M HCl aqueous solution (80 µL), additive NaTPB (1 mg) and ionophore TCA (4 mg) were mixed in a sample tube, and the mixture was then allowed to stand at 80 °C for 1 h to afford a viscous sol–gel solution. The clean graphite electrode was then coated by viscous sol–gel solution and allowed to dry for 48 h at room temperature. The electrodes were then rinsed with water and conditioned in 0.1 mol dm-3 vanadyl sulfate solution.

4. Static mode potentiometric measurements

The sol–gel and PVC membrane containing TCA were used as the measuring electrode in conjunction with saturated calomel electrode (Azar Electrode Co., Urmia, Iran). All measurements were preformed at ambient temperature (25 ± 1 °C) using a pH/mV meter (Metrohm, 691). The performance of each electrode was investigated by measuring its potential in prepared solutions at concentration ranging from 5.0 × 10-8 to 1.0 × 10-1 mol dm-3 by serial dilution at constant pH. The potentiometric cell for PVC membrane was: Ag–AgCl / 3 mol dm-3 KCl / internal solution (1.0 × 10-3 mol dm-3 VO2+ + 0.185 mol dm-3 HCl + 0.20 mol dm-3 CH3COONa) // PVC membrane // sample solution / bridged electrolyte / Hg–Hg2Cl2, KCl (sat'd) and for the sol–gel electrode potentiometric cell was: Hg, Hg2Cl2, KCl (sat'd) || sample test | sol–gel | C electrode (graphite(

The EMF readings were made after the potential reached a constant value. The activity coefficients (γ) were calculated according to the Debye–Hückel procedure [27], however, for the calibration curve, concentration was used instead of activity.

RESULTS AND DISCUSSION

1. Study of the interaction between calix[4](O_3S_2-crown-5)ether and VO^{2+} ions

In order to obtain evidence of the coordination of TCA with VO^{2+} ion and determination of ionophore toVO^{2+} mole ratio, the values of conductivity of 5.0 × 10^{-4} mol dm^{-3} $VOSO_4$ in acetonitrile solution were monitored as a function of TCA to VO^{2+} mole ratio at 25 °C and the results are plotted in Fig. 1.

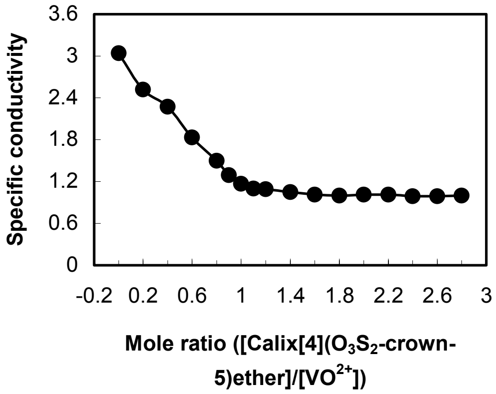


Fig.1. Plot of conductivity vs. [calix[4](O_3S_2-crown-5)ether]/[VO^{2+}] in acetonitrile solutions.

It is seen that the addition of the TCA to VO^{2+} solution causes a significant decrease in conductivity which tends to level off at mole ratio about one. The complexation of TCA with a number of cations was also conductometrically investigated which Table 1 exhibits the formation constants, K_f, of the resulting 1:1 complexes. It is seen that the TCA with the most stable complex of VO^{2+} ion is expected to act as a highly selective ionophore for preparation of VO^{2+} ion-selective membrane electrodes. Thus, in the next step, the TCA was used as a potential neutral carrier in construction of sol-gel derived membrane ion-selective electrodes for vanadylion.

Table 1. Formation constants of different M^{n+}-ionophore complexes in acetonitrile.

Cation	Log K_f	Cation	Log K_f
VO^{2+}	4.38 ± 0.11	Fe^{2+}	2.18 ± 0.17
Fe^{3+}	3.08 ± 0.10	Mg^{2+}	1.89 ± 0.15
Cs^{+}	3.36 ± 0.08	Al^{3+}	2.16 ± 0.12
Ni^{2+}	1.34 ± 0.13	Ca^{2+}	1.74 ± 0.05
Cd^{2+}	1.22 ± 0.07	Ba^{2+}	1.02 ± 0.09
Cu^{2+}	2.11 ± 0.09	Pb^{2+}	2.71 ± 0.15
Cr^{3+}	1.05 ± 0.13		

2.Optimization of sol-gel membranes preparation

In order to test the performance of the electrodes characteristics, various operation parameters viz. selectivity, response time, sensitivity, lifetime, working range of the electrodes at different concentrations of the metal ion, pH and the effect of the membranes composition were investigated.

The vanadyl-selective electrodes show Nernstian response in a wide concentration ranging from 1.0×10^{-6} to 1.0×10^{-1} mol dm^{-3} and 1.0×10^{-5} to 1.0×10^{-1} mol dm^{-3} for sol-gel and PVC membrane sensors, respectively. Fig. 2 shows a typical potential response for the vanadyl-selective electrodes based on PVC membrane and sol–gel ion sensor.

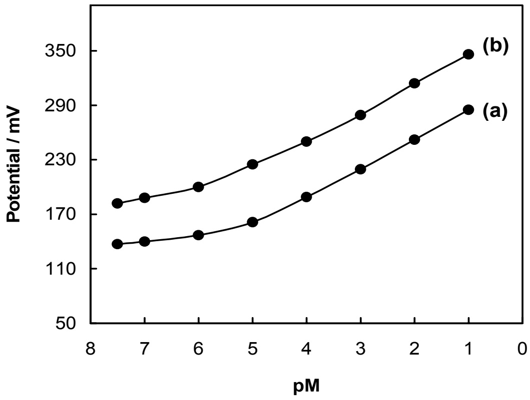


Fig.2. Calibration graph for the VO^{2+}- ISE by (a) PVC membrane and (b) sol-gel sensor.

The potential response of all the electrodes using membranes of thiacalix[4]arene of different composition based on PVC and sol-gel was investigated by varying the concentration of the test solution from 5.0×10^{-8} to 1.0×10^{-1} mol dm^{-3} and the obtained results are given in Table 2.

As shown in Table 2, the use of 62% DBS in the presence of 3% TCA and 5% KTpClPB and 30% PVC results in acquiring the best sensitivity with a Nernstian slope of 28.4 ± 0.6 mV/decade over a relatively wide concentration range of VO^{2+} ions for PVC membrane and the characteristics performance of the electrode was the best (No. 5b). For sol-gel sensor, the use of 250 μl DEDMS, 90 μl TEOS, 280 μl ethanol and 80 μl HCl 0.1 mol dm^{-3}, at the presence of 4 mg TCA and 1 mg NaTPB, results the best response with a Nernstian slope of 29.3 ± 0.3 mV/decade over a relatively wide concentration range of VO^{2+} ions and the best sensor was No. 2a.

The lifetime of the electrodes was determined by recording its potential at an optimum pH value and plotting its calibration curve each day. It was observed that there was no significant change in the slope of the electrode on the following day. The PVC membrane electrode was tested over a period of 2 months to investigate its stability which the electrode was in daily use during this period. The parameters, such as the slope, working range and response time of the electrode were found to be reproducible. The sol–gel electrode was also tested over a period of 6 months to investigate its stability and the analytical parameters were found to be reproducible during this period.

Table 2. The composition and characteristics of several typical membranes for sol-gel and PVC membrane electrodes

(a) Sol-gel sensor

No.	TEOS (µL)	DEDMS (µL)	HCl (µL)	Ethanol (µL)	Additive (mg)	TCA (mg)	Slope (mV/decade)	Linear range (mol dm^{-3})
1	90	250	80	280	KTpClPB, 1	4	24.5	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$
2	90	250	80	280	NaTPB, 1	4	29.3	$1.0 \times 10^{-6} – 1.0 \times 10^{-1}$
3	100	250	80	280	NaTPB, 1	4	27.4	$1.0 \times 10^{-6} – 1.0 \times 10^{-1}$
4	90	250	80	280	NaTPB, 1	3	20.4	$1.0 \times 10^{-6} – 1.0 \times 10^{-1}$
5	90	250	80	280	NaTPB, 1	5	33.7	$1.0 \times 10^{-6} – 1.0 \times 10^{-1}$
6	90	250	80	280	NaTPB, 0.5	4	25.8	$1.0 \times 10^{-6} – 1.0 \times 10^{-1}$
7	90	250	80	280	---	4	25.2	$1.0 \times 10^{-4} – 1.0 \times 10^{-1}$
8	90	250	80	280	NaTPB, 1	---	18.4	$1.0 \times 10^{-4} – 1.0 \times 10^{-1}$

(b) PVC membrane

No.	PVC (mg)	TCA (mg)	Plasticizer (mg)	Additive (mg)	Slope (mV/decade)	Linear range (M)
1	30	5	AP, 60	OA, 5	25.5	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$
2	30	5	AP, 60	KTpClPB, 5	35.1	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$
3	30	3	AP, 62	KTpClPB, 5	32.8	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$
4	30	3	2-NPOE, 62	KTpClPB, 5	31.9	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$
5	30	3	DBS, 62	KTpClPB, 5	28.4	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$
6	30	---	DBS, 62	KTpClPB, 5	14.9	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$
7	30	3	DBS, 62	---	16.1	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$
8	0	---	DBS, 62	---	11.4	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$

The limit of detection defined as the concentration of vanadyl ion obtained when extrapolating the linear region of the calibration plot to the base-line potential was about 4.9 × 10-7 and 3.1 × 10-6 mol dm-3 for sol–gel sensor and PVC membrane, respectively.Optimum conditioning time for the vanadyl-selective electrodes in 1.0 × 10-1 mol dm-3 vanadyl sulfate solution was found to be 24 and 48 h for PVC and sol–gel electrode, respectively. It then generated stable potential when placed in contact with VO2+ solutions.

3. Effect of pH

The influence of the pH of the test solution on the potential response of the PVC membrane and sol-gel electrodes at the presence of 1.0×10^{-3} mol dm^{-3} of VO^{2+} solution in the pH range of 0.0–6.0 by adjusting the pH of the test solution with HCl was investigated (Fig. 3). As shown in Fig. 3, the potential remains constant within pH range of 3.0 – 6.0 for both electrodes, but between 0.0 and 3.0, a drastic decrease is observed. The observed change in potential response at lower pH values (pH < 3) may be due to the protonation of the ionophore or the responding of the electrodes to H^+ as an interfering species which results in an increased potential of the system by increasing concentration of proton in solution [28]. Therefore, for settlement of this problem, from buffer solution built up CH_3COONa and HCl with pH of 3.5 were used. Based on bourbaix diagram, more details about the effect of pH on other species of vanadium ion were previously reported [29].

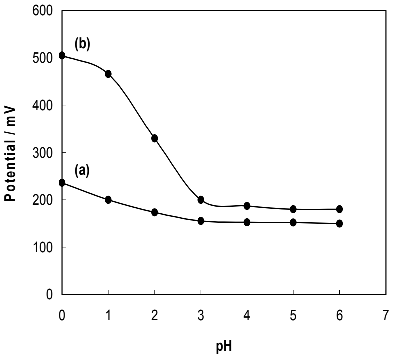


Fig.3. The pH response of the VO^{2+}- ISE by (a) PVC membrane and (b) sol-gel sensor.

4. Potentiometric selectivity pattern

The basic parameter characterizing the analytical properties of each new electrode is its selectivity coefficient. Therefore, the coefficients of selectivity should be determined in a standardized way by a theoretically justified method which ensures the analytical usefulness of the values determined and enables the possibility of comparison of selectivity's of different electrodes.

The selectivity of the PVC and sol-gel electrodes in presence of various cations was evaluated by the fixed primary ion method at 1.0×10^{-3} mol dm^{-3} concentration of vanadylion.

$$K^{pot}_{I,J} a_J^{Z_I/Z_J} = a_I\{\exp[(E_2 - E_1)\frac{F}{RT}]\} - a'_I \qquad (1)$$

where a_J is the activity of the interfering ion, E_1 is the potential measurement when only I is present, E_2 is the potential response to the primary ion at the presence of interfering ion, $K^{pot}_{I,J}$ is the selectivity coefficient and Z_I, Z_J are the charges of I and J. For the determination of the selectivity coefficients, the potential of 1.0×10^{-3} mol dm^{-3} vanadyl solution were measured (E_1) at first, then in the presence of 10^{-4}, 10^{-3}, 10^{-2} and 0.1 mol dm^{-3} of interfering ions the potential values were recorded (E_2) once more. The $a_J^{Z_I/Z_J}$ values were plotted against the right hand side of Eq. (1) and the slope will be equal to the selectivity coefficient of the interfering ion. From the potentiometric selectivity data presented in Table 3, it is observed that thiacalix[4]arene interacts relatively strongly with VO^{2+} ions and can be successfully used as a sensing agent for vanadyl-selective electrodes. This behavior may be due to the selective uptake of vanadyl by thiacalix[4]arene in comparison to the other species listed in Table 3.

Table 3. Selectivity coefficient of various interference ions for VO^{2+}- ISE by PVC membrane and sol-gel sensor

	Selectivity coefficients ($K^{Pot}_{VO^{2+},M}$)	
M^{n+}	Sol-gel sensor	PVC membrane
Al^{3+}	2.92×10^{-3}	3.26×10^{-3}
Cr^{3+}	2.04×10^{-4}	5.93×10^{-3}
Fe^{2+}	5.75×10^{-6}	8.44×10^{-4}
Pb^{2+}	1.07×10^{-5}	4.28×10^{-3}
Ba^{2+}	3.49×10^{-3}	4.51×10^{-3}
Cd^{2+}	1.85×10^{-5}	4.76×10^{-3}
Ni^{2+}	2.49×10^{-3}	2.17×10^{-3}
Cu^{2+}	2.92×10^{-2}	3.27×10^{-2}
Mg^{2+}	2.41×10^{-4}	3.52×10^{-3}
Zn^{2+}	6.56×10^{-2}	2.10×10^{-2}
Ca^{2+}	4.44×10^{-2}	5.54×10^{-2}
Fe^{3+}	2.59×10^{-1}	7.82×10^{-3}
Co^{2+}	1.62×10^{-2}	8.68×10^{-4}
NH_4^+	2.17×10^{-4}	9.0×10^{-1}
Na^+	1.62×10^{-1}	9.32×10^{-1}
Li^+	2.71×10^{-2}	9.97×10^{-1}
Cs^+	1.02×10^{-1}	1.58
Tl^+	2.74×10^{-4}	7.38

Of course, from comparing data in Table 3 we can see that the electrodes based on PVC and sol-gel exhibit almost the same selectivity toward vanadyl ion; however, the potentiometric selectivity coefficients of the sol-gel sensor for hard metal ions as lead, chromium(III), cadmium and iron(II) ions are better than those of the PVC electrode. The results show some ions that are strongly interference for PVC membrane, such as Tl^+, Li^+ and NH_4^+, are not interference for sol-gel electrode. Of course, in some cases, such as iron(III) and Co^{2+}, selectivity coefficients are better for PVC electrode.

A perusal of selectivity coefficient data presented in Table 3 indicates that the PVC electrode is sufficiently selective over a large number of cations except Na^+, Li^+, Cs^+, Tl^+, and NH_4^+. Table 3 also shows that the electrode based on sol–gel exhibits suitable selectivity for vanadyl ion over a large number of cations except Na^+, Cs^+ and Fe^{3+}. The results show that Na^+ and Cs^+ ions are interference for both electrodes.

5. Response time

The response time of an ISE is the length of time between the instant at which the ISE and a reference electrode are brought into contact with a sample solution (or the time at which the concentration of the ion of interest in a solution is changed by contacting with an ISE and a reference electrode) and the first instant at which the potential of the cell becomes equal to its steady state value within ±1 mV or has reached 90% of the final value. In this study, the practical response time was recorded by changing solution with different VO^{2+} concentrations from 1.0×10^{-4} to 1.0×10^{-2} mol dm^{-3}. The results showed that both electrodes reach the equilibrium response in a short time of about 15 s.

6. Effect of temperature

Trend of changes of electrodes performance with temperature , at test solution temperatures 20, 25, 30, 40 and 50 °C for the PVC membrane and sol-gel electrode are presented in Table 4. The electrodes exhibit good Nernstian behavior at the temperature range of 20 – 50 °C. The standard cell potentials ($E°_{cell}$) were determined at different temperatures from the respective calibration plots as the intercepts of these plots at $-\log [VO^{2+}] = 0$, and were used to determine the isothermal temperature coefficient ($dE°/dt$) of the cell with the aid of the following equation [30]:

$$E^0_{cell} = E^0_{cell}(25^0 C) + (\frac{dE}{dt})_{cell}(t-25) \qquad (2)$$

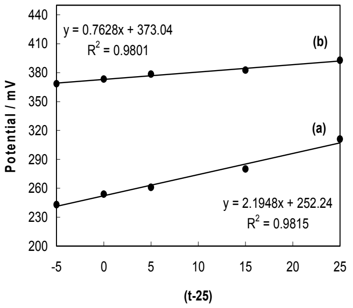


Fig.4. Variation of standard potential of the cell for (a) PVC membrane and (b) sol-gel electrode.

Plot of $E°_{cell}$ versus (t - 25) produced a straight line for both electrodes as shown in Fig. 4. The slopes of these lines were taken as the isothermal temperature coefficient of the cell which are 0.00219 V/°C and 0.00076 V/°C for PVC and sol-gel electrodes, respectively.

The standard potentials of the reference electrode were calculated using the following equation:

$$E^0_{Hg,Hg_2Cl_2} = 0.241 - 0.00066(t-25) \qquad (3)$$

The values of the standard potentials of vanadyl-electrodes were calculated at the different temperatures from the following relation:

$$E^0_{cell} + E^0_{reference} = E^0_{electrode} \qquad (4)$$

Plot of $E°_{electrode}$ versus (t - 25) gave straight lines which the slope was taken as the isothermal temperature of coefficient of the vanadyl electrodes. Those amounts are 0.0015 V/°C and 0.00014 V/°C for PVC membrane and sol-gel electrodes, respectively. The small values of $(dE/dt)_{cell}$ and $(dE/dt)_{electrode}$ reveal the high thermal stability of the electrodes within the investigated temperature range. However, temperature coefficients show that the thermal stability of sol-gel electrode is more than that of PVC membrane.

Table 4. Trend of changes of electrodes performance with temperature for PVC membrane and sol-gel electrode

Temperature (°C)	Slope (mV/decade)	E° (mV)	Linear range (mol dm^{-3})
(a) PVC membrane			
20	27.9	244.7	1.0×10^{-1} to 1.0×10^{-5}
25	28.4	268.9	1.0×10^{-1} to 1.0×10^{-5}
30	29.1	270.1	1.0×10^{-1} to 1.0×10^{-5}
40	30.6	292.4	1.0×10^{-1} to 1.0×10^{-5}
45	33.0	301.3	1.0×10^{-1} to 5.0×10^{-5}
50	34.9	317.8	1.0×10^{-1} to 5.0×10^{-5}
(b) Sol-gel			
20	27.8	368.6	1.0×10^{-1} to 1.0×10^{-6}
25	29.3	373.3	1.0×10^{-1} to 1.0×10^{-6}
30	31.0	378.4	1.0×10^{-1} to 1.0×10^{-6}
40	32.6	382.6	1.0×10^{-1} to 1.0×10^{-6}
50	33.6	392.8	1.0×10^{-1} to 1.0×10^{-6}

7. Analytical application

The proposed electrodes were successfully applied to the determination of VO^{2+} ions in some synthetic samples. Several spiked samples were prepared by adding aliquots (a few micro liters) of VO^{2+} solution to Li^+, Cr^{3+} and Fe^{3+} solutions, according to Table 5, and the results are shown in Table 5.

Table 5. Potentiometric determination of VO2+ ions in various spiked samples by the PVC membrane and sol-gel electrode

Spiked (ppm)				Sol-gel		PVC membrane	
VO^{2+}	Li^+	Cr^{3+}	Fe^{3+}	Found VO^{2+} (ppm)	Recovery (%)	Found VO^{2+} (ppm)	Recovery (%)
8.5	4	---	---	8.67	102	9.12	107.3
8.5	---	3	---	8.37	98.5	8.46	99.5
8.5	---	---	2	9.07	106.7	8.39	98.7
8.5	4	3	---	8.63	101.5	9.09	106.9
8.5	4	---	2	9.18	108	9.54	112.2
8.5	---	3	2	9.10	107.1	8.81	103.6
8.5	4	3	2	9.41	110.7	9.71	114.2

The results show that the PVC electrode can be successfully used at presence of Cr^{3+} and Fe^{3+} but the electrode response is destroyed by presence of Li^+ In fact, it seems that there is a matrix effect in spiked samples so that the interference of Li^+ in response function is relatively high as expected from its high selectivity coefficient (Table 3). Of course, the higher concentration of Li^+ (4 ppm) to Cr^{3+} (3 ppm) and Fe^{3+} (2 ppm) in spiked samples increases its interference effect (Table 5). The results also show that the sol-gel electrode can be used at presence of Cr^{3+} and Li^+, but presence of Fe^{3+} is interference for electrode response as expected from its high selectivity coefficient (Table 3).

CONCLUSION

The obtained results of present work demonstrate that the thiacalix[4]arene as a suitable ionophore can be used in developing of PVC-based ion-selective and sol-gel electrodes. The electrodes response to the VO^{2+} ions in a Nernstian fashion with low detection limits especially in the case of sol-gel electrode. The results show that the thermal stability of sol-gel electrode is more than that of PVC membrane. The electrodes are characterized by a fast response, a reasonable long-term stability and low cost. Table 6 lists linear range, detection limit, lifetime, response time and slope of some of the vanadyl-selective electrodes against proposed vanadyl-selective electrodes for comparative purposes [14-16, 31,32].

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Table 6. Comparison of a VO^{2+}-selective electrodes based on TCA with those previously reported in literature

Reference	Slope (mV/decade)	Response time (s)	Lifetime	Detection limit(mol dm^{-3})	Linear range (mol dm^{-3})
[14]	29.1	15	---	---	7.9×10^{-6} to 1.0×10^{-1}
[15]	29.7 ± 0.25	<10	5 weeks	7.9×10^{-6}	1.0×10^{-5} to 1.0×10^{-1}
[16]	29.9	15	2 month	3.9×10^{-6}	1.0×10^{-5} to 1.0×10^{-1}
[32]	29.5	<10	--	1.0×10^{-6}	1.0×10^{-5} to 1.0×10^{-2}
[33]	29.7 ± 0.25	10	---	7.9×10^{-6}	1.0×10^{-5} to 1.0×10^{-1}
Proposed (PVC)	28.4 ± 0.6	<15	2 month	3.1×10^{-6}	1.0×10^{-5} to 1.0×10^{-1}
Proposed (sol-gel)	29.3 ± 0.3	<15	6 month	4.9×10^{-7}	1.0×10^{-6} to 1.0×10^{-1}

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