

**Preparation and Application of Al<sup>3+</sup> - Sensor Based On (2Z) – Methyl 2 – ((z) (p-tolylimino) -3-Ethyl –4-Oxothiazolidin – 5 – Ylidene Acetate in PVC Matrix**

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**ABSTRACT**

Al<sup>3+</sup>-Potentiometric sensor, based on (2Z) –methyl 2– ((z) (p-tolylimino)-3-ethyl –4-oxothiazolidin – 5– ylidene) Acetate (MTEOY) as a neutral ionophore, was successfully developed for the detection of Al<sup>3+</sup> in aqueous solutions. The electrode responds to Al<sup>3+</sup> ion with a sensitivity of  $19.8 \pm 0.1$  mV/decade over the range  $1.0 \times 10^{-8}$ –  $1.0 \times 10^{-1}$  mol L<sup>-1</sup> and in a pH range of 3.0–9.0. The electrode shows a detection limit of  $3.5 \times 10^{-9}$  mol L<sup>-1</sup>. The influence of membrane composition, the pH of the test solution, and the interfering ions on the electrode performance was investigated. The proposed electrode shows good discrimination of Al<sup>3+</sup> ion from several cations. The effect of temperature on the electrode response shows that the temperature higher than 50 °C deteriorates the electrode performance. The electrode was found to work well under laboratory conditions. This sensor not only was used in determination of Al<sup>3+</sup> in real samples but also was used to determination of Al<sup>3+</sup> concentration in the presence of certain interfering ions.

**Keywords:** Al<sup>3+</sup>-selective electrode; Modified separate solution method; Neutral carrier; Potentiometry

**INTRODUCTION**

In the area of membrane-based Ion Selective Electrodes (ISEs), emphasis has been focused on the development of new ionophores and on the composition of the membrane phase, aiming at enhancing the potentiometric responses of the ISEs. Fabrication of a new, ion-specific ISE with high selectivity and sensitivity, wide linear concentration range, long lifetime, good reproducibility and low cost, is always in need [1]. The introduction of new ion-selective membrane electrodes has played a fundamental role in the development of potentiometric measurements. The advantages of ISEs over many other methods

are their easy handling, non-destructive analysis and inexpensive sample preparation.

Interest and concern about aluminum has considerably increased in recent years, due to the knowledge about the potential toxic effects of this element. Although there is no reported cases of acute aluminum poisoning of healthy individuals exposed to normal levels of aluminum, several studies have been published relating aluminum exposure and age related neurological disorders, such as Alzheimer's disease [2].

The determination of Al<sup>3+</sup> ion has been carried out directly or indirectly by a variety

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of instrumental methods. These methods include inductively coupled plasma-atomic emission spectrometry (ICP-AES) [3-7], liquid chromatography [8], stripping voltammetry [9] and graphite furnace atomic absorption spectrometry [10].

However, in comparison with other toxic metal cations, very few electrodes have been reported for the estimation of  $Al^{3+}$  in solution [11-18]. All the reported electrodes generally have relatively acceptable performance for monitoring  $Al^{3+}$  but they suffer from some limitations, such as relatively poor selectivity [17], low dynamic range ( $5.0 \times 10^{-6}$  to  $1.0 \times 10^{-2}$  M) [13] and high detection limit [16]. Therefore, it is obvious that there is still a need for developing better sensor for  $Al^{3+}$  ion. Electrically neutral lipophilic ligands containing the appropriate number of binding sites of high dipole moment and high polarizability could be employed as ion-active phase for metal ions. The design and synthesis of new macrocyclic ligands for specific analytical applications is a subject of continuous interest [19, 20].

The purpose of the present work is the development of a  $Al^{3+}$ -selective electrode based on a poly (vinyl chloride) (PVC) membrane of (2Z) - methyl 2 - ((z) (p-tolylimino) -3-ethyl -4-oxothiazolidin- 5-ylidene) Acetate (MTEOY) as an ionophore. To the best of our knowledge this compound has not previously been used in the development of an  $Al^{3+}$ -selective electrode or in any other ion-selective electrode.

## EXPERIMENTAL

### Reagents

Reagent grade acetophenone (AP), oleic acid (OA), tetrahydrofuran (THF), high relative molecular weight PVC (all from Merck), EtNCS,  $PhNH_2$ , Dimethyl Azo Dicarboxylate (DMAD),  $CH_3COONa$  and absolute EtOH (from Fluka or Aldrich) were used as

received. Chloride and nitrate salts of all other cations (all from Merck) were of the highest purity available and used without any further purification. Double distilled deionized water was used throughout.

### Synthesis of ionophore (MTEOY)

MTEOY (Fig.1) was synthesized under following conditions: At first, EtNCS (1 mmol) was added to a solution of  $PhNH_2$  (1 mmol) in ethanol (10 ml) followed by the addition of DMAD (1.2 mmol) and  $CH_3COONa$  (0.3 mmol) at ambient temperature, produced the desired product that recrystallization in hot ethanol gave as sole product in excellent yields (yield: 89%).

Yield 89%, Yellow solid, m.p.98-100 °C, FT-IR (KBr):  $\nu$  ( $cm^{-1}$ ): 3065, 2980, 1716, 1692, 1630, 1610,  $^1H$  NMR (500 MHz,  $CDCl_3$ , 25°C):  $\delta$ =1.34 (t, 3H, J= 7 Hz), 2.3 (s, 3H), 3.8 (s, 3H), 4.0 (q, 2H, J= 7 Hz), 6.8 (d, 2H, J= 8.2 Hz), 6.9 (s, 1H), 7.2 (d, 2H, J= 8.2Hz).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ , 0, 25°C):  $\delta$ =12.8, 20.7, 38.0, 52.8, 116.1, 120.7, 129.7, 134.8, 141.9, 144.6, 151.2, 164.6, 166.3.

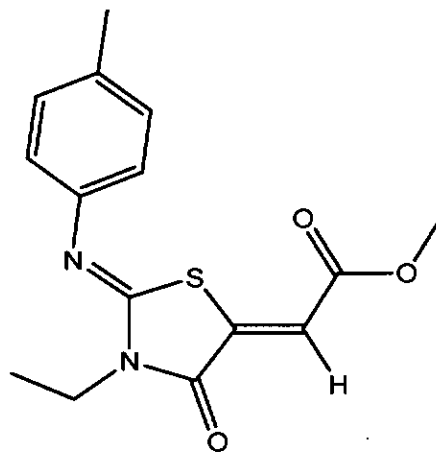


Fig. 1. Chemical scheme of (2Z)-methyl 2- ((z) (p-tolylimino) -3-ethyl -4-oxothiazolidin - 5 - ylidene) Acetate (MTEOY) used as ionophore.

### Preparation of membrane

Membranes containing different compositions were studied and the optimum

found was 32.0 wt. % of powdered PVC, 57 wt. % of plasticizer (AP), 8 wt. % of additive (OA) and 4 wt. % of the corresponding ionophore (MTEOY). These were mixed in 2.0 ml of THF. The solvent was evaporated slowly until an oily concentrated mixture was formed. A Pyrex tube (4 mm o.d.) was dipped into the mixture for about 15 s so that a transparent membrane of about 0.4 mm thickness was formed. The tube was then pulled out from the solution and kept at room temperature for about 2h. The tube was then filled with internal solution  $1.0 \times 10^{-4}$  M  $Al^{3+}$ . The electrode was finally conditioned for 24 h by soaking in a  $1.0 \times 10^{-3}$  M  $La^{3+}$  solution. The ratios of various ingredients, concentration of equilibrating solution and time of contact were optimized to provide a membrane that was reproducible, noiseless and stable potential.

### Potential measurement

Potentials were measured with a Corning ion analyzer pH/mV meter relative to a double junction saturated calomel electrode (SCE) with the chamber filled with an ammonium nitrate solution at constant temperature ( $25 \pm 0.1$  °C). A silver / silver chloride electrode containing a 3 M solution of KCl was used as the internal reference electrode. The electrode cell assembly of the following type was used: Ag-AgCl | KCl (3 M) | internal solution,  $1.0 \times 10^{-4}$  M  $Al^{3+}$  | PVC membrane | test solution | Hg-Hg<sub>2</sub>Cl<sub>2</sub>, KCl (saturated).

## RESULTS AND DISCUSSION

### Effect of membrane composition on the electrode response

The potential responses of various ion-selective electrodes are shown in Fig. 2. Except for the  $Al^{3+}$  ion-selective electrode, in all other cases the slope of the corresponding potential-pM plots is much lower than the expected Nernstian slopes.

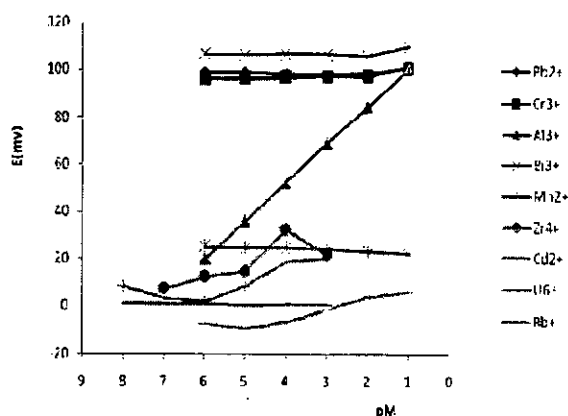


Fig. 2. Potential response of various ion-selective membranes based on MTEOY.

Taguchi's design methodology [21] has wide ranging applications. In the Taguchi method the results of the experiments are analyzed to achieve one or more of the following three objectives:

1. To establish the best or the optimum condition for a product or a process
2. To estimate the contribution of individual factors
3. To estimate the response under the optimum conditions

The power and popularity of the method lies in the discipline rather than the technique itself. The composition of membrane was optimized by Taguchi method in order to achieve better slope. The resulting values of the slope are summarized in Table 1. It is seen that the membrane having a composition as PVC: AP: OA: MTEOY as 32:57:8:4 wt. % exhibits the best results.

In this work, the effect of four important factors including amount of PVC, AP, MTEOY, OA and each factor at five levels were studied using Taguchi's method. In the proposed method, no interaction between the variables was found in the matrix and the focus was placed on the main effects of the four most important factors. ANOVA was used to evaluation of results. The ANOVA [21] results (Table 2) showed that the most important factor contributing to the response of sensor was MTEOY (91.3%) followed by AP (2.3%).

**Table 1.** The composition and characteristics of several typical membranes for  $Al^{3+}$ -electrodes

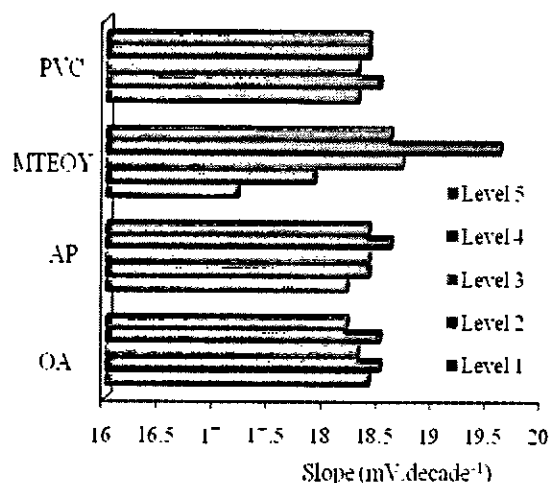
No.	Pvc(mg)	AP(mg)	MTEOY (mg)	OA(mg)	Slope mV/decade	Linear range (M)	R2
1	26	57	2	2	17.0	$1.0 \times 10^{-6}$ – $5.0 \times 10^{-1}$	0.90 01
2	28	59	2	4	17.3	$1.0 \times 10^{-6}$ – $5.0 \times 10^{-1}$	0.93 16
3	30	61	2	6	17.1	$1.0 \times 10^{-6}$ – $5.0 \times 10^{-1}$	0.94 02
4	32	63	2	8	17.5	$1.0 \times 10^{-6}$ – $1.0 \times 10^{-1}$	0.95 00
5	34	65	2	10	17.2	$1.0 \times 10^{-6}$ – $1.0 \times 10^{-1}$	0.95 05
6	28	57	4	6	17.5	$5.0 \times 10^{-7}$ – $5.0 \times 10^{-1}$	0.97 21
7	30	59	4	8	17.8	$2.5 \times 10^{-7}$ – $5.0 \times 10^{-1}$	0.96 90
8	32	61	4	10	18.1	$2.5 \times 10^{-7}$ – $1.0 \times 10^{-1}$	0.97 44
9	34	63	4	2	17.9	$5.0 \times 10^{-7}$ – $1.0 \times 10^{-1}$	0.95 89
10	26	65	4	4	18.0	$5.0 \times 10^{-7}$ – $5.0 \times 10^{-1}$	0.91 99
11	30	57	6	10	18.5	$1.0 \times 10^{-7}$ – $1.0 \times 10^{-1}$	0.98 03
12	32	59	6	2	18.8	$1.0 \times 10^{-7}$ – $2.5 \times 10^{-1}$	0.92 20
13	34	61	6	4	18.2	$5.0 \times 10^{-7}$ – $5.0 \times 10^{-2}$	0.97 80
14	26	63	6	6	19.0	$1.0 \times 10^{-7}$ – $1.0 \times 10^{-2}$	0.92 15
15	28	65	6	8	19.1	$5.0 \times 10^{-7}$ – $1.0 \times 10^{-2}$	0.98 00
16	32	57	8	4	19.8	$1.0 \times 10^{-8}$ – $1.0 \times 10^{-1}$	0.97 96
17	34	59	8	6	19.6	$5.0 \times 10^{-8}$ – $5.0 \times 10^{-1}$	0.99 98
18	26	61	8	8	19.5	$1.0 \times 10^{-8}$ – $5.0 \times 10^{-1}$	0.98 45
19	28	63	8	10	19.6	$5.0 \times 10^{-8}$ – $1.0 \times 10^{-1}$	0.97 41
20	30	65	8	2	19.3	$5.0 \times 10^{-7}$ – $5.0 \times 10^{-1}$	0.93 09
21	34	57	10	8	18.2	$1.0 \times 10^{-7}$ – $1.0 \times 10^{-1}$	0.98 54
22	26	59	10	10	18.5	$1.0 \times 10^{-7}$ – $1.0 \times 10^{-1}$	0.95 32
23	28	61	10	2	18.9	$5.0 \times 10^{-7}$ – $1.0 \times 10^{-1}$	0.96 04
24	30	63	10	4	19.0	$1.0 \times 10^{-7}$ – $1.0 \times 10^{-1}$	0.94 01
25	32	65	10	6	18.4	$1.0 \times 10^{-7}$ – $1.0 \times 10^{-1}$	0.90 25

**Table 2.** ANOVA results for experimental responses in the OA<sub>25</sub> matrix

Factor	D. F.	S	V	P (%)
PVC	4	0.282	0.0705	1.624
AP	4	0.408	0.102	2.350
MTEOY	4	15.86	3.965	91.359
OA	4	0.056	0.014	0.3226
Error	4	0.754	0.1885	4.343
Total	24			

D. F.; Degrees of freedom, S; Sum of squares, V; Variance, P (%); Percent contribution

To take full advantages of the procedure, various experimental parameters must be studied to obtain an optimized system. These parameters were optimized in the present research by a four-factor five-level factorial design and the experimental data were evaluated using Qualitek4 Software. The mean values of the five levels of each factor revealed how the membrane sensitivity changes when the level of that factor changes. Fig.3 shows the slope as a function of the levels of the studied factors.

**Fig. 3.** Slope variation as a function of the levels of the studied factors.

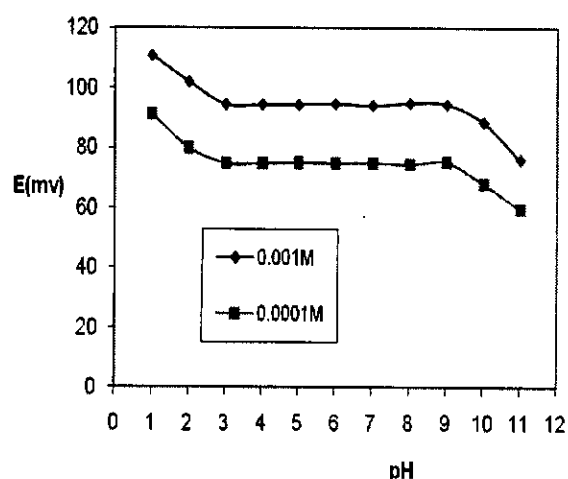
#### Influence of internal reference solution

The working of membrane electrode in relation to variation of reference solutions was investigated. It was found that, the variation of the concentration of the internal solution from  $10^{-1}$  to  $10^{-4}$  mol  $l^{-1}$  of  $Al^{3+}$  solution did not cause any significant difference in potential response except for an expected change in the

intercept of the resulting plots. Therefore a solution of  $10^{-4}$  M  $Al^{3+}$  would be used as a suitable internal solution.

#### Effect of pH

The effect of pH on the response of the electrode was studied over the pH range from 1 to 11 at different concentrations ( $10^{-3}$  to  $10^{-4}$  M) of  $Al^{3+}$  solution. The pH of solutions was adjusted with either HCl or NaOH solutions. Potential remains constant at pH range from 3 to 9 (Fig. 4). Below pH 3, the change in the potential is due to co fluxing of hydrogen ions and above pH 9, the variation of potential may be due to formation of some hydroxyl complex of the  $Al^{3+}$  ions in solution.

**Fig. 4.** Effect of pH at  $1.0 \times 10^{-3}$  and  $1.0 \times 10^{-4}$  M  $Al^{3+}$  solutions on the potential response of membrane no. 16.

#### Response time, lifetime and reversibility

The response time of the electrodes, tested by measuring the time required to achieve a steady potential (within  $\pm 1$  mV), was less than 5 s and was sustained for about 10 min over the linear range of the concentration (Fig. 5). The detection system was very stable, and after a period of 3 months, calibration sensitivity decreased about 1.4 mV without any considerable change in its linear range. The reproducibility of the slope of calibration graphs was within  $\pm 0.5$  mV per decade over a period of 3 months ( $n = 16$ ).

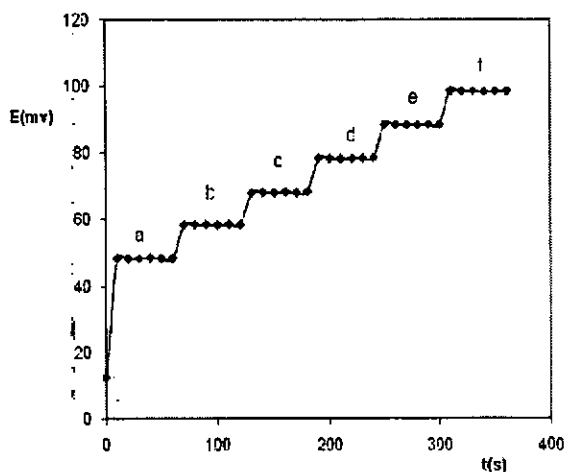


Fig. 5. Dynamic response of membrane electrode for step change in concentration of  $Al^{3+}$ ; (a)  $1.0 \times 10^{-5}$ , (b)  $5.0 \times 10^{-5}$ , (c)  $1.0 \times 10^{-4}$ , (d)  $5.0 \times 10^{-4}$ , (e)  $1.0 \times 10^{-3}$ , (f)  $5.0 \times 10^{-3}$  M.

Reversibility is an important factor for an ion-selective electrode. Fig. 6 shows that the potentiometric response of the electrode is reversible, although the times needed to reach equilibrium values were longer than that of low-to-high sample concentrations [21]. The detection limit, taken at the point of intersection of the extrapolated linear segment of the calibration curve, was  $3.5 \times 10^{-9}$  M.

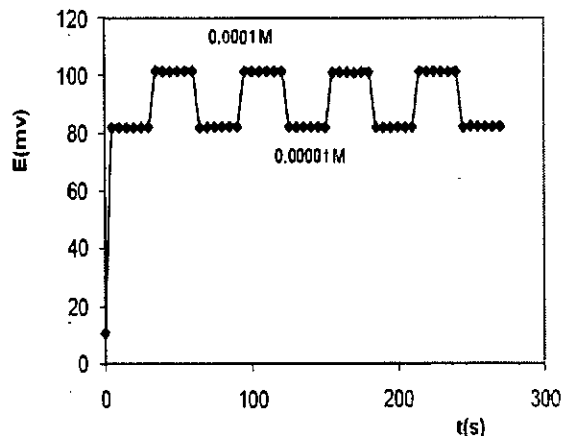


Fig. 6. Dynamic response characteristics of the  $Al^{3+}$ -electrode for several high-to-low sample cycles.

### Selectivity

The influence of interfering ions on the response behavior of ion-selective membrane electrode is usually described in terms of selectivity coefficient ( $K_{Al,j}$ ). The

potentiometric selectivity coefficients  $K_{Al,j}$  of electrode were evaluated by matched potential method [22] and modified separate solution method (MSSM) [23, 24].

The resulting values of the selectivity coefficients are summarized in Table 3 and Table 4. It is evident from the selectivity coefficients data, that the sensor exhibits a high performance for  $Al^{3+}$  ion compared with alkali, alkaline earth, transition and heavy metal ions.

Table 3. Selectivity coefficients ( $K_{Al,j}$ ) of various ions with  $Al^{3+}$ -selective electrode, determined by MPM

Interfering ion	$-\log k^{pot}_{Sr,j}$	Interfering ion	$-\log k^{pot}_{Sr,j}$
$Cu^{2+}$	4.41	$Fe^{3+}$	5.41
$Mn^{2+}$	5.90	$Cr^{3+}$	5.12
$Ni^{2+}$	5.61	$Tl^{+}$	5.89
$Pb^{2+}$	5.40	$K^{+}$	5.98
$Zn^{2+}$	3.90	$Na^{+}$	6.00
$Hg^{2+}$	4.67	$Ce^{3+}$	5.94
$Ca^{2+}$	4.90	$La^{3+}$	5.31
$Mg^{2+}$	6.00	$Sr^{2+}$	5.92
$Cd^{2+}$	5.12	$Li^{+}$	5.70
$Co^{2+}$	4.33	$Ag^{+}$	5.18
$Ba^{2+}$	5.80	$NH_4^{+}$	5.83

Table 4. Selectivity coefficients ( $K_{Al,j}$ ) of various ions with  $Al^{3+}$ -selective electrode, determined by MSSM

Interfering ion	$-\log k^{pot}_{Sr,j}$	Interfering ion	$-\log k^{pot}_{Sr,j}$
$Cu^{2+}$	6.05	$Fe^{3+}$	5.90
$Mn^{2+}$	7.18	$Cr^{3+}$	5.95
$Ni^{2+}$	6.20	$Tl^{+}$	7.00
$Pb^{2+}$	5.71	$K^{+}$	7.50
$Zn^{2+}$	5.95	$Na^{+}$	7.31
$Hg^{2+}$	5.40	$Ce^{3+}$	5.83
$Ca^{2+}$	6.36	$La^{3+}$	5.60
$Mg^{2+}$	7.20	$Sr^{2+}$	5.98
$Cd^{2+}$	6.34	$Li^{+}$	6.60
$Co^{2+}$	5.42	$Ag^{+}$	5.88
$Ba^{2+}$	6.50	$NH_4^{+}$	5.90

Comparison of the main analytical features of some the previously described  $\text{Al}^{3+}$  ion selective electrodes [11-18] with the proposed sensor revealed that; the present electrode exhibited a better selectivity (Table 5).

#### Effect of non-aqueous media

The functioning of the electrode was investigated in partially non-aqueous media using acetone–water, acetonitrile–water, methanol–water and ethanol–water mixtures and the results obtained are presented in Table 6. It is observed that in the presence of acetonitrile and acetone, the slope decreases remarkably. The slope is acceptable in the presence of ethanol and methanol until about 30% (v/v) in the water and for the higher percentage of ethanol, the slope decreases. Therefore, the electrode is not suitable for using in acetone–water and acetonitrile–water mixtures. However, in ethanol–water

and methanol–water mixture (up to 30%), there is only a small decrease in slope and working concentration range and hence the electrode can be satisfactorily used in these media with above-mentioned percentages.

#### Effect of temperature

Trend of changes of electrode performance with temperature, at test solution temperatures 10, 20, 30, 40, 50 and 60 °C for the  $\text{Al}^{3+}$ -electrode was studied. The electrode exhibits good Nernstian behavior in the temperature range (10–50 °C). At higher temperatures, the slope of electrode did not show a good Nernstian behavior. This behavior may be due to the disturbances occurring in phase boundary equilibrium at the PVC layer-test solution interface produced by the thermal agitation of the solution. The standard cell potentials ( $E^0_{\text{cell}}$ ), were determined at different

**Table 5.** Comparison of the potentiometric selectivity coefficient obtained by MPM and MSSM with previously reported sensors

Interfering ion	Ref. [17]	Ref. [18]	Ref. [13]	Ref. [16]	Ref. [12] <sup>a</sup>	Ref. [12] <sup>b</sup>	This work	
							MSSM	MPM
$\text{Mn}^{2+}$	-----	2.51	3.13	3.602	5.05	4.44	7.18	5.9
$\text{Pb}^{2+}$	4.02	2.73	2.54	3.096	3.337	2.72	5.71	5.4
$\text{Zn}^{2+}$	3.92	2.01	2.58	3.55	1.79	1.136	5.95	3.9
$\text{Fe}^{3+}$	-----	2.54	2.36	2.408	3.25	3.25	5.90	5.41
$\text{Cr}^{3+}$	-----	3.07	3.16	2.698	-----	-----	5.95	5.12
$\text{K}^+$	3.38	3.17	2.8	3	3.2	1.013	7.50	5.98
$\text{Na}^+$	3.16	3.05	2.54	2.769	4.346	1.95	7.31	6.00
$\text{Ce}^{3+}$	-----	2.67	4.02	-----	4.92	4.92	5.83	5.94
$\text{Sr}^{2+}$	-----	-----	2.57	-----	3.148	2.508	5.98	5.92
$\text{Li}^+$	-----	-----	2.39	-----	3.455	1.065	6.60	5.70
$\text{Ag}^+$	-----	-----	2.11	-----	3.88	1.468	5.88	5.18

<sup>a</sup> SSM

<sup>b</sup> MSSM

temperatures from the respective calibration plots as the intercepts of these plots at  $pAl = 0$ , and were used to determine the isothermal temperature coefficient ( $dE^0/dt$ ) of the cell with the aid of the following equation [25, 26]:

$$E^0_{\text{cell}} = E^0_{\text{cell}}(25^\circ\text{C}) \pm (dE^0/dt)_{\text{cell}}(t - 25)$$

Plot of  $E^0_{\text{cell}}$  versus  $(t - 25)$  produced a straight line. The slope of this line was taken as the isothermal temperature coefficient of the cell. It amounts to  $0.000590 \text{ V}/^\circ\text{C}$ . The standard potentials of the reference electrode ( $\text{Hg}/\text{Hg}_2\text{Cl}_2; \text{KCl}$  (saturated)) were calculated using the following equation:

$$E^0_{\text{Hg}/\text{Hg}_2\text{Cl}_2} = 0.241 - 0.00066(t - 25)$$

The values of the standard potentials of  $\text{Al}^{3+}$ -electrodes were calculated at the different temperatures from the following relation:

$$E^0_{\text{cell}} + E^0_{\text{reference}} = E^0_{\text{electrode}}$$

Plot of  $E^0_{\text{electrode}}$  versus  $(t - 25)$  gave a straight line. The slope of the line was taken as the isothermal temperature coefficient of the  $\text{Al}^{3+}$ -electrode. It amounts to  $0.0000589 \text{ V}/^\circ\text{C}$ . The small values of  $(dE^0/dt)_{\text{cell}}$  and  $(dE^0/dt)_{\text{electrode}}$  reveal the high thermal stability of the electrode within the investigated temperature range.

### Analytical application

The performance of the sensor no.16 was further investigated to determine aluminum in Tap water, Mineral water, Al-Mg syrup and industrial waste water. The results are found to be close agreement with those obtained by AAS (Table 7). Thus, the sensor can be employed for  $\text{Al}^{3+}$  Quantification in real samples.

**Table 6.** Performance of the membrane sensor in partially non-aqueous media

Non aqueous content %(v/v)	Slope (mV/decade)	DLR (M)
Acetone		
10	19.7	$1.0 \times 10^{-8}$ to $1.0 \times 10^{-1}$
20	19.6	$1.0 \times 10^{-8}$ to $1.0 \times 10^{-1}$
30	15.0	$1.0 \times 10^{-6}$ to $1.0 \times 10^{-1}$
40	12.9	$1.0 \times 10^{-5}$ to $5.0 \times 10^{-1}$
Methanol		
10	19.8	$1.0 \times 10^{-8}$ to $1.0 \times 10^{-1}$
20	19.7	$1.0 \times 10^{-8}$ to $1.0 \times 10^{-1}$
30	19.5	$5.0 \times 10^{-8}$ to $1.0 \times 10^{-1}$
40	16.7	$1.0 \times 10^{-7}$ to $1.0 \times 10^{-1}$
Ethanol		
10	19.7	$1.0 \times 10^{-8}$ to $1.0 \times 10^{-1}$
20	19.6	$1.0 \times 10^{-8}$ to $1.0 \times 10^{-1}$
30	19.6	$1.0 \times 10^{-7}$ to $1.0 \times 10^{-1}$
40	16.2	$5.0 \times 10^{-5}$ to $1.0 \times 10^{-1}$
Acetonitrile		
10	19.6	$1.0 \times 10^{-8}$ to $1.0 \times 10^{-1}$
20	19.4	$2.5 \times 10^{-8}$ to $1.0 \times 10^{-1}$
30	17.5	$1.0 \times 10^{-7}$ to $1.0 \times 10^{-1}$
40	15.9	$1.0 \times 10^{-5}$ to $1.0 \times 10^{-1}$



**Table 7.** Determination of Al<sup>3+</sup> ions in different samples by AAS and proposed sensor

Sample	Aluminum content <sup>a</sup>	
	Al <sup>3+</sup> -Sensor	AAS method
Tap water <sup>b</sup>	$5.1 \times 10^{-5}$	$5.6 \times 10^{-5}$
Mineral water <sup>c</sup>	$5.3 \times 10^{-4}$	$4.9 \times 10^{-4}$
Mineral water <sup>d</sup>	$5.2 \times 10^{-4}$	$4.7 \times 10^{-4}$
Al-Mg Syrup	$7.8 \times 10^{-3}$	$7.0 \times 10^{-3}$
Waste water <sup>e</sup>	$2.9 \times 10^{-5}$	$3.6 \times 10^{-5}$

<sup>a</sup>: Average of three measurements

<sup>b</sup>: Spiked with  $5 \times 10^{-5}$  M Al<sup>3+</sup>

<sup>c</sup>: Spiked with  $5 \times 10^{-4}$  M Al<sup>3+</sup>

<sup>d</sup>: Spiked with  $5 \times 10^{-4}$  M Al<sup>3+</sup>

<sup>e</sup>: Prepared from Rash Industrial Zone

## CONCLUSIONS

On the results discussed in this paper, (2Z) – methyl 2 – ((z) (p-tolylimino ) -3-ethyl-4-oxothiazolidin – 5– ylidene ) Acetate (MTEOY) can be considered as a suitable neutral ionophore for construction of a PVC-based membrane selective electrode for the direct determination of Al<sup>3+</sup> ion in solution. The proposed electrode responds to Al<sup>3+</sup> in a Nernstian fashion and presents high selectivity and sensitivity to Al<sup>3+</sup> ion, relatively wide dynamic range, low detection limit, long lifetime and fast response time. The proposed electrode reveals excellent selectivity for Al<sup>3+</sup> over a wide variety of alkali, alkaline earth, some transitions, and

heavy metal ions. The electrode performs successfully in partially non aqueous medium. The proposed Al<sup>3+</sup> ion-selective electrode was found to work well under laboratory conditions and it was successfully applied to the determination of Al<sup>3+</sup> ions in real samples.

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