

Construction and Characterization of Indium Liquid Ion Selective Electrodes Based on Crown Ethers in a PVC Matrix Membrane

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Several indium ion selective electrodes were constructed based on 15-crown-5 (15C5), dicyclohexano-18-crown-6 (DCH18C6) and dibenzo-24-crown-8 (DB24C8) as sensors and di-octyl phenyl phosphonate (DOPP), di-butyl phthalate (DBPH), tri-butyl phosphate (DBP), tri-n-amyl phosphate (TAP) and bis (2-ethyl hexyl) phosphate (BEHP) as plasticizers in a PVC matrix membrane. Electrode parameters, pH effect and interferences were also studied.

The indium electrode based on 15C5 using DOPP as a plasticizer gave the best response for low levels of In³⁺ ions. The linear range for this electrode ranged from 3.8 x 10⁻⁵ to 5.0 x 10⁻² M (with correlation coefficient r = 0.9997), the slope was 20.1 mV/decade with a detection limit of 1.2 x 10⁻⁵ M, and the working pH range was 3.8–5.9.

Interferences of Na⁺, K⁺, NH₄⁺, Ca²⁺, Ba²⁺, Cd²⁺, La³⁺, Nd³⁺ and Eu³⁺ on the electrode response were also investigated using a mixed solution method. Mono- and divalent cations were found to interfere less than trivalent cations.

The concentrations of indium ions in the prepared standard solutions were determined by direct, standard addition (SA), multiple standard addition (MSA) and titration methods. The results were compared with those obtained by atomic absorption spectrophotometry. The precision and accuracy of each method were calculated and expressed in terms of the relative standard deviation and the relative error.

Optical measurements were also studied by measuring the absorbance for each membrane after steady intervals of immersion in a standard solution of its ions using UV/Visible spectrophotometry. Each membrane showed a rapid decrease in absorbance when it reached the end of its life due to leaching of the membrane contents to the external solution.

Key Words: Indium electrodes, crown compounds, selectivity measurements, optode measurements.

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Introduction

Ion selective electrodes based on a neutral carrier have provided an acceptable, sensitive, selective and conveniently inexpensive method of analyzing of rare earth ions¹. Some of these electrodes are highly sensitive to particular rare earth ions but often lack the selectivity and linearity range required for the individual determination of rare earth ions in a multicomponent system. A selective separation of lanthanides by supported liquid membranes containing Cyanex 925 as a carrier was reported by Garcia-Valls et al.². The membrane under certain conditions is shown to be effective for the transport and separation of lanthanides.

Didarul et al.³ have constructed samarium(III) selective electrodes based on bis (alkyl xanthano) alkanes and bis (thia alkyl xanthano) alkynes, where both compounds showed a good response toward Sm(III) ions. The electrodes give a slope of 22 mV/ decade, a detection limit of 5.0×10^{-7} M and a linear range of $1.0 \times 10^{-1} - 5 \times 10^{-3}$ M. Electrodes based on crown ether compounds were also constructed for the determination of other heavy metal ions such as uranyl ions⁴. Nassory and Karim⁵ have reported the construction of uranyl electrodes based on 18-crown-6, dibenzo-18-crown-6 and dicyclohexano-18-crown-6 with different plasticizers. The detection limit of these electrodes was 2.0×10^{-4} M, the slope was about 30 mV/decade and the linear range extended from 10^{-2} to 10^{-4} M.

Indium is classified as a rare element with an oxidation state of 3+ and is quite stable to atmospheric exposure. One of the early uses of indium was in the coating of other elements to protect them against wear and corrosion. It also has uses in alloys, in semiconductors and as a solder to metal⁶. Stark et al.⁷ prepared an indium(III) chloride complex with 12-crown-4 and distinguished it by single X-ray diffraction. Fujinawa et al.⁸ have prepared a support liquid membrane for indium and used it in metallurgic recovery of gallium and indium.

Kondo et al.⁹ separated indium and gallium by a supported liquid membrane containing diisostearyl phosphoric acid and indium was selectively permeated through the liquid membrane. Li and Hou¹⁰ constructed and evaluated a novel In(III) liquid ion selective membrane electrode based on a complex of In(III) 1-benzyl-3-methyl-4-benzoyl-5- pyrazolone and diphenylguanidine.

Optical chemical sensors, also called optodes, can make use of a homogeneous membrane similar to the polymeric membrane used for potentiometric chemical sensors¹¹. The bulk optode is typically based on PVC or similar polymers and exploit the high selectivity of the same lipophilic ionophores that are employed in ion selective membranes¹².

The aim of this study was to construct and characterize several ion selective electrodes for the potentiometric determination of indium ions. These electrodes are based on several crown ethers and plasticizers. The best compatibility of crown ether, plasticizer and PVC matrix was chosen for the indium. The electrode parameters, pH and selectivity were investigated. An optical study was performed for the membranes in order to demonstrate the mechanism of the mobility of the ions.

Experimental part

Equipment

1. Expandable ion analyzer, Orion model EA 940.
2. pH meter, model PHM-82 Radiometer Copenhagen.

3. Combined glass electrode type Orion 91-02 Swiss made.
4. Calomel reference electrode type Gallenkam.
5. Atomic absorption spectrophotometer, Shimadzu type AA 670.
6. Double beam UV-Vis spectrophotometer type Shimadzu UV-160.

Reagents and solutions

Crown compounds 15-crown-5 (15C5), dicyclohexano-18-crown-6 (DCH18C6) and dibenzo-24-crown-8 (DB24C8) were obtained from Fluka. Plasticizers, di-octyl phenyl phosphonate (DOPP), di-butyl phthalate (DBPH), tri-butyl phosphate (TBP), tri-amyl phosphate (TAP) and bis(2-ethyl hexyl) phosphate (BEHP) were obtained from Fluka and Aldrich. Stock solution of 0.1 M indium chloride was prepared in deionized water acidified with HCl.

Stock solutions of 0.1 M NaCl, KCl, NH₄Cl, BaCl₂, CaCl₂, CdCl₂, LaCl₃, EuCl₃ and Nd(NO₃)₃ were also prepared. The other standard solutions were prepared from the stock solutions.

All other chemicals and reagents used in this study were of analytical grade obtained from different companies.

Deionized bi-distilled water was used throughout the experimental work.

Procedure

Preparation of indium picrate complexes with crown ethers:

Following the same procedure given in the literature¹³ for the preparation of indium picrate and the complex with crown compounds obtained by adding 15 mL of acetone containing 1 mmol of 15C5 to 10 mL of acetone containing 1 mmol of In(Pic)₃ salt. After reflux at 60 °C for 30 min, a yellow precipitate was obtained.

Other complexes with DC18C6 and DB24C8 were prepared using the same procedure except that the solvent was 1:1 ethanol – dichloroethane mixture.

Assembly of the electrode

Construction of the electrode body and the immobilization of crown ether complexes in the PVC matrix membrane were done using the method given by Craggs et al.¹⁴.

The glass tube was ³/₄ filled with 0.01 M InCl₃ solution. The membrane was immersed in a standard solution of 0.1 M of the same ion for about 24 h before using it for measurements.

Electrode response

The potential was measured for standard solutions at different pH levels from 1 to 12 where the pH was adjusted with NH₄OH and HCl. A calibration curve was constructed with concentrations ranging from 10⁻⁶ to 10⁻¹ M. The curves were plotted on Orion 7 cycle-logarithmic graph paper. The selectivity was determined by mixed solution method (14).

Sample determination

Three synthetic samples of different concentrations were prepared for In(III) ion. The concentrations of these samples were determined using direct, standard addition (SA), Gran's plot and titration methods. A Gran's plot was performed on a special Orion semi-antilog graph paper (10% correction) by plotting electrode potential versus the added standard ^{15,16}.

A potentiometric precipitation titration was also applied as a comparative method. In this method 100 mL of sample solution of 0.1 M In(III) was titrated with 5×10^{-2} M NaOH.

Optical measurements

A UV-Vis absorbance measurements were performed for each membrane after steady time intervals. The absorbance of each membrane was plotted against the time of immersion.

Results and Discussion

Fifteen newly prepared sensors based on PVC membranes were constructed using In(III) picrate complexes with 15-crown-5, dicyclo-18-crown-6 and dibenzo-24-crown-8 dissolved in different plasticizers. The electrode parameters for these electrodes including slope, detection limit, linear range, correlation coefficient (*r*) and life time are listed in Table 1.

Table 1. Properties of indium selective electrodes using different crown compounds and plasticizers.

Electrode no.	Plasticizer	Crown compound	Slope mV/decade	Detection limit/M	Linear con. range/M	Corr. coeff. <i>r</i>	Life time/day
1	DOPP	15C5	20.1	1.2×10^{-5}	3.8×10^{-5} - 5.0×10^{-2}	0.9997	55
2	DOPP	DCH18C6	19.3	1.5×10^{-5}	4.5×10^{-5} - 3.8×10^{-2}	0.9984	40
3	DOPP	DB24C8	18.8	2.2×10^{-5}	6.5×10^{-5} - 3.5×10^{-2}	0.9995	14
4	DBPH	15C5	26.1	2.4×10^{-5}	6.0×10^{-5} - 4.5×10^{-2}	0.9998	16
5	DBPH	DCH18C6	22.8	5.0×10^{-5}	5.0×10^{-5} - 3.3×10^{-2}	0.9994	11
6	DBPH	DB24C8	25.4	3.5×10^{-5}	7.0×10^{-5} - 2.7×10^{-2}	0.9993	9
7	TBP	15C5	18.5	2.5×10^{-5}	7.0×10^{-5} - 6.0×10^{-2}	0.9996	8
8	TBP	DCH18C6	18.5	1.8×10^{-5}	5.5×10^{-5} - 8.0×10^{-2}	0.9992	6
9	TBP	DB24C8	18.9	1.6×10^{-5}	5.0×10^{-5} - 5.0×10^{-2}	0.9988	3
10	TAP	15C5	21.4	2.7×10^{-5}	7.0×10^{-5} - 4.0×10^{-2}	0.9982	15
11	TAP	DCH18C6	21.3	1.8×10^{-5}	6.5×10^{-5} - 3.0×10^{-2}	0.9993	12
12	TAP	DB24C8	20.9	1.8×10^{-5}	5.5×10^{-5} - 2.4×10^{-2}	0.9994	8
13	BEHP	15C5	32.7	1.2×10^{-4}	2.6×10^{-4} - 4.0×10^{-2}	0.9995	18
14	BEHP	DCH18C6	31.7	1.7×10^{-4}	4.0×10^{-4} - 4.0×10^{-2}	0.9989	15
15	BEHP	DB24C8	31.2	2.0×10^{-4}	5.5×10^{-4} - 3.5×10^{-2}	0.9996	15

The calibration curves for In-selective electrodes containing 15C5, DCH18C6 and DB24C8 as sensors and DOPP as a plasticizer gave an excellent linear range (Table 1). The In-electrode using 15-crown-5 and DOPP plasticizer has a wider linear range than other 2 In-electrodes based on other crown ethers. This is due to the compatibility between the components of the membrane. Figure 1 shows the calibration curves of the indium electrode based on crown ethers and DOPP as a plasticizer.

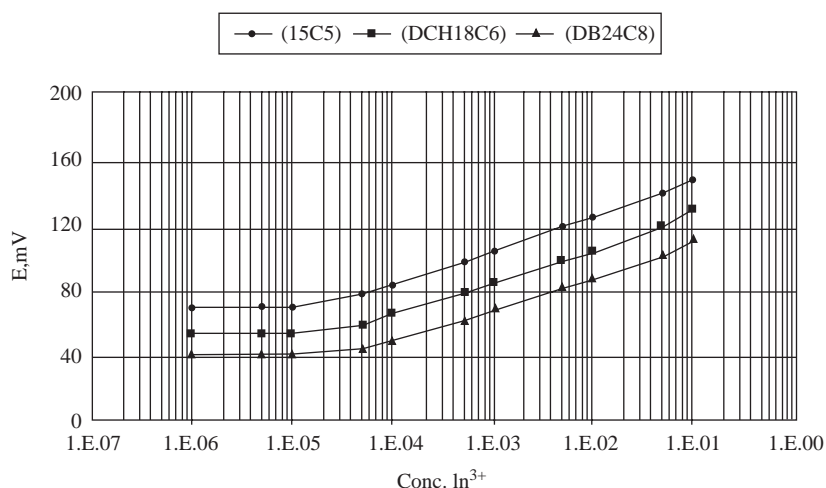


Figure 1. Calibration curves for indium - ISEs containing 15C5, DCH18C6 and DB24C8 crown ether compounds using DOPP as a plasticizer.

The concentration of the internal filling solution for all the constructed electrodes varied from 10^{-3} to 10^{-1} M In(III) and the electrode's responses were measured throughout the linear range. The best results were obtained at 10^{-2} M internal solution. The results of electrode parameters show that the electrode based on 15C5 and DOPP as a plasticizer gives a better response for In(III) than the In-electrodes using DCH18C6 and DB24C8, in which the slope was around 20.1 mV/decade and the detection limit 1.2×10^{-5} M.

The In-electrodes based on membranes using DBPH as a plasticizer have good linearity (Table 1) with slopes of 26.1, 22.8 and 25.4 mV/decade for membranes nos. 4, 5 and 6.

From the results obtained, the electrodes based on DBPH as a plasticizer were considered more sensitive than the electrodes based on DOPP because of their higher slope values compared with slope values of the electrodes using DOPP. The electrodes based on TBP as a plasticizer gave Nernstian slopes similar to the electrodes based on DOPP plasticizer; however, their life times were shorter, making them less applicable. This could be due to the low viscosity of TPB (3.114 cST) compared with that of DOPP (16.7 cST), which causes rapid leaching of the complex out of the membrane when it is in contact with aqueous solution. The slope values for the In-electrodes using TAP plasticizer are relatively close to the Nernstian slope but their life times are relatively short.

The calibration curves for In-electrodes using BEHP have a shorter linear range (Table 1) than the other electrodes studied in the range 10^{-4} to 10^{-2} M. The slopes of the electrodes based on BEHP as a plasticizer were far from the Nernstian slope value, but still gave a response to indium and can be used for indium measurements. Figure 2 shows the calibration curves for indium electrodes based on crown ethers and BEHP as a plasticizer.

The effect of pH on the electrode response was investigated. The working pH ranges for the In-electrodes using different plasticizers were determined and are listed in Table 2.

Above these pH values responses gradually deviate from the normal values. This may be due to the formation of $\text{In}(\text{OH})_3$, which has been found to limit rare earth determination by other analytical methods.

The working pH range for In-electrodes based on BEHP had a wider pH range of performance compared with the electrodes based on other plasticizers. This may be attributed to the presence of acidic

hydrogen in BEHP and this may reduce the hydrolysis of In(III) ions in solution at higher pH values.

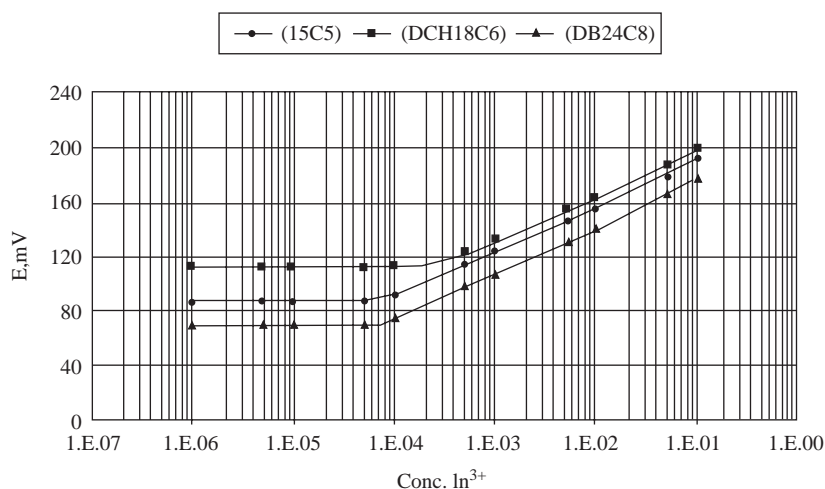


Figure 2. Calibration curves for indium - ISEs containing 15C5, DCH18C6 and DB24C8 crown ether compounds using DBPH as a plasticizer.

Table 2. Working pH range for In-electrodes using different crown compounds and different plasticizers.

Electrode no.	Plasticizer	Crown compound	pH range
1	DOPP	15C5	3.85.9
2	DOPP	DCH18C6	4.05.8
3	DOPP	DB24C8	3.86.1
4	DBPH	15C5	3.96.0
5	DBPH	DCH18C6	4.16.2
6	DBPH	DB24C8	3.96.4
7	TPB	15C5	3.65.8
8	TPB	DCH18C6	3.55.8
9	TPB	DB24C8	3.45.9
10	TPA	15C5	3.65.5
11	TPA	DCH18C6	3.45.9
12	TPA	DB24C8	3.26.1
13	BEHP	15C5	4.16.2
14	BEHP	DCH18C6	4.36.0
15	BEHP	DB24C8	4.36.5

The response time for In-electrodes generally ranged from 25 s to 7 min. The electrodes based on DCH18C6 and DB24C8 using DOPP as a plasticizer attained a steady response time for equilibrium after \approx 30 s and \approx 60 s for solutions 1.0×10^{-1} and 1.0×10^{-5} M, respectively. The electrode with 15C5 using DOPP reached equilibrium after 40 s and 100 s for solutions of 1.0×10^{-1} and 1.0×10^{-5} M, respectively. These differences in the response time may be due to the large cavity size of ligands DCH18C6 and DB24C8, which facilitates adaptation and causes the quick release of M^{3+} ions. This would suggest that additional oxygen donor atoms introduced into the crown ether ring increase the binding of M^{3+} ions inside the membrane phase¹⁷. The response time for membranes based on DBPH plasticizer, 30 s to 90 s for concentrations of 10^{-1} and 10^{-5} M, were similar to those based on DOPP plasticizer. This may be due to the comparable

viscosities of the 2 plasticizers. For TBP the response time ranged from 20 s to 90 s. This may be due to the low viscosity (3.114cST), which increases the mobility of the complex inside the membrane.

The calibration curves for In-electrodes were checked for drift (parallel drift, the slope of the calibration does not change with time). A drift of 7 mv on the calibration curve of the In-electrode after 12 and 20 days was observed, as shown in Figure 3 for membrane no.1.

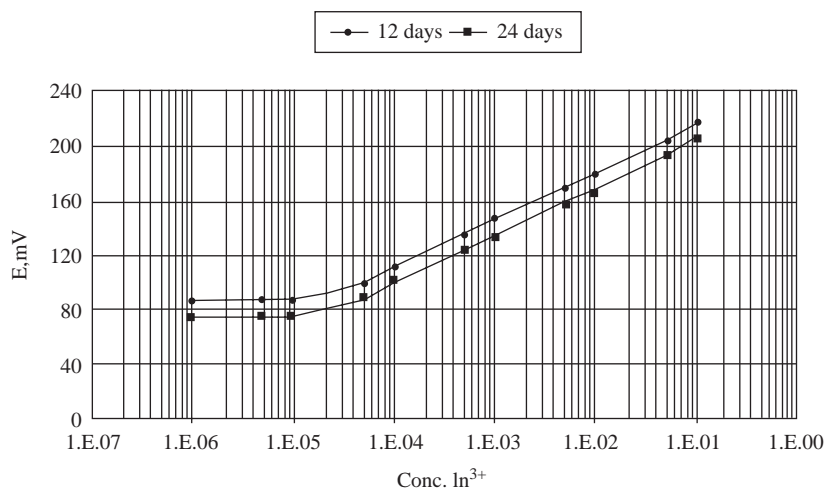


Figure 3. Calibration curves for membrane no. 1 after 12 and 20 days. Shift in curves with constant slope.

Interferences of Na^+ , K^+ , NH_4^+ , Ca^{2+} , Ba^{2+} , Cd^{2+} , Nd^{3+} , La^{3+} and Eu^{3+} on the electrode response were investigated. A mixed solution method was used, and the potentials for a series of standard solutions containing different concentrations of the indium ions with a fixed concentration of the interfering ion were measured for In-electrodes based on 15C5, DCH18C6 and DB24C8 ethers using DOPP as a plasticizer were examined. The ratios of interfering ions are listed in Table 3 for each ion with respect to each electrode.

Table 3. Maximum allowable ratios of interfering ion (10^{-3} M) to indium ion (10^{-4} M) for electrode based on 15C5 and DOPP.

crown ether	Maximum allowable ratio interference								
	Na^+	K^+	NH_4^+	Ca^{2+}	Ba^{2+}	Cd^{2+}	La^{3+}	Nd^{3+}	Eu^{3+}
15C5	79	82	83	63	71	45	35	27	31
DCH18C6	80	79	81	50	61	39	2.5	2.0	1.5
DB24C8	86	72	86	50	40	55	8.0	9.0	10

The electrode based on 15C5 showed better selectivity than those based on DCH18C6 and DB24C8 for In(III) over the larger La(III). The variation in the ratio of selectivity for mono-,divalent and trivalent cations was due to the cation-cavity size relationship.

However, the smallest ion Eu(III) was found to interfere with In(III) more than La(III), where the ratios were 31, 1.5 and 10 for In-electrodes based on 15C5, DCH18C6 and DB24C8, respectively.

Sample analysis

The concentrations of In(III) ions in prepared standard solutions were determined using an In-electrode based on 15C5 and DOPP as a plasticizer using direct, standard addition (SA), multiple standard addition (MSA) and titration methods.

Good results were obtained using the direct method where the RE% did not exceed 2.3% with RSD% not more than 2.5%.

In the standard addition method, the concentrations of indium ions are 10^{-3} , 8×10^{-4} and 6×10^{-4} M, respectively. The plot of antilog. E/S versus the volume of the multiple addition of the standard solution was used to determine the concentration of In(III). A typical plot is shown in Figure 4.

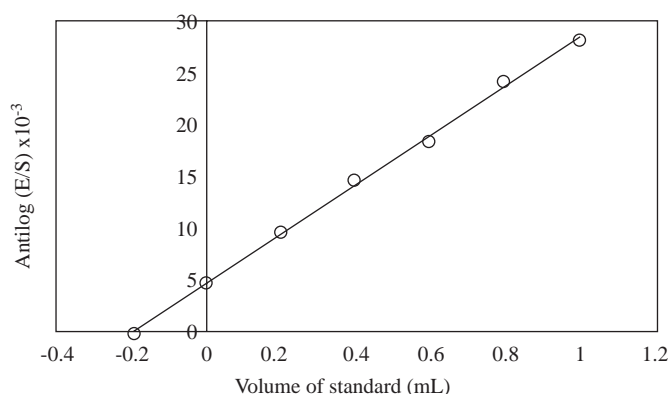


Figure 4. Antilog E/S versus volume of the added standard for determination of In(III) in sample solution 0.001 M by MSA method.

In the titration method a Gran's plot was constructed using Gran's plot paper. Three concentrations of indium ions were used (10^{-3} , 8×10^{-4} and 6×10^{-4} M), titrated with 0.05 M NaOH. A typical Gran's plot is shown in Figure 5.

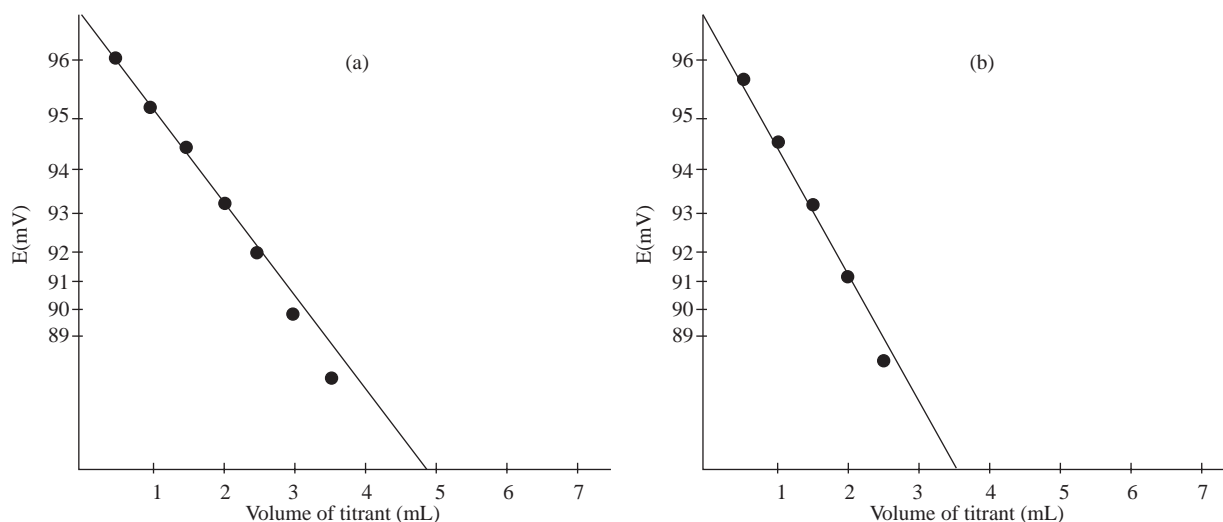


Figure 5. Gran's plot for the determination of In(III) in solution against 0.05 M NaOH, a: sample solution of 8×10^{-4} M, b: sample solution of 6×10^{-5} M.

The RSD and RE values obtained by SA and MSA methods were very comparable with the values obtained by atomic absorption as shown in Table 4.

Optical measurements

Each membrane is immersed in 1.0×10^{-3} M of In(III) solution for a period of time, and absorbance measurements for each membrane are performed after steady time intervals of soaking. The absorbance for each membrane began to decrease to an extent depending on the stability of the complex and its compatibility with the plasticizer used.

Table 4. Indium ion samples using In-electrode (membrane no. 2) comparing with atomic absorption.

Calculated conc. /M	Measured concentration /M using potentiometric methods				
	Atomic abs. method	Direct	SA	MSA	Titration
1.0×10^{-3}	0.992×10^{-4}	0.979×10^{-3}	1.02×10^{-3}	1.004×10^{-3}	0.958×10^{-3}
RSD%	1.06	2.06	1.43	1.12	2.29
RE%	0.80	2.10	2.00	0.40	4.20
8.0×10^{-4}	7.970×10^{-4}	8.019×10^{-4}	7.98×10^{-4}	8.007×10^{-4}	8.033×10^{-4}
RSD%	1.21	2.25	1.52	1.31	2.70
RE%	0.38	0.23	0.25	0.10	0.41
6.0×10^{-4}	5.964×10^{-4}	5.984×10^{-4}	6.01×10^{-4}	6.01×10^{-4}	5.95×10^{-4}
RSD%	1.21	2.31	1.60	1.32	3.12
RE%	0.60	0.27	0.17	0.17	0.83

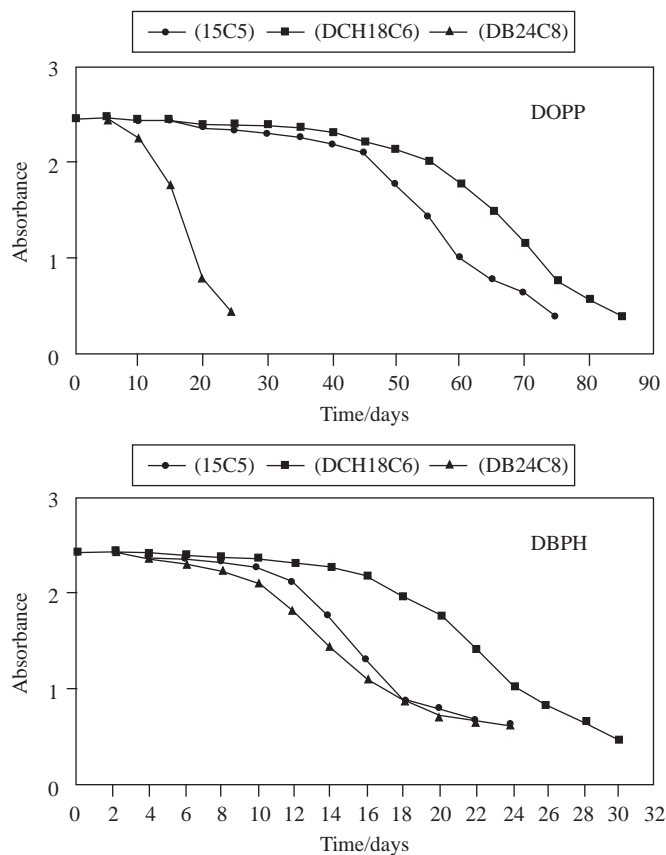


Figure 6. Absorbance of In-membranes based on DOPP and DBPH plasticizers and different crown ethers versus time after soaking the membranes in 0.001 M indium chloride.

The absorbance for each membrane decreased more rapidly after a period of time nearly consistent with the end of its life time. Figure 6 shows the decrease in the absorbance with time for indium electrodes based on DOPP and DBPH as plasticizers with the 3 crown compounds.

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