

## Gallium Selective PVC Membrane Electrodes Based on Crown Ethers

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### Abstract

Gallium selective electrodes based on 12-crown-4 (12C4) and benzo-15-crown-5 (B15C5) and plasticizers dioctyl phenyl phosphonate (DOPP), dibutyl phosphate (DBP), dibutyl phthalate (DBPH) in PVC matrix membranes are constructed. Specific properties of the electrodes are studied including calibration curve, slope, detection limit, concentration range, response time and life time as well as the effect of pH on electrode response. Interference for  $\text{Li}^{1+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$  on electrode response have been also investigated. The polymeric liquid membrane electrode based on 12C4 using DBPH plasticizer exhibits the best over all performances as a gallium selective electrode over a wide concentration range ( $1.0 \times 10^{-5}$  –  $3.3 \times 10^{-2}$  M) with Nernstian slope (20mV/decade). It has a relatively fast response time excellent detection limit ( $7 \times 10^{-6}$  M) and good durability (about 2 months). The electrode revealed a good selectivity for  $\text{Ga}^{3+}$  over a variety of other metal ions and could be used in a pH range of 3.0-5.0. It was used as an indicator electrode in potentiometric titration of gallium ions.

### Introduction

The increasing number of investigations about ion selective electrodes have been done in the last decade because of their ease in use and their selectivity characteristics. Many of these selective electrodes are prepared with organic ion-exchangers having large sized molecules and with neutral carriers. These membranes are sensitive to a large number of ions than the glass and solid state membranes. Among

these  $\text{Ca}^{2+}$ ,  $\text{K}^{+}$  and  $\text{NO}_3^{-}$  ion electrodes are commercially available (1-3). The first liquid ion-exchanger membrane electrode was prepared by Ross in 1967(4) using phosphate esters as the active material. This electrode was used for the determination of calcium in blood serum. The liquid membrane electrodes show long response times and low selectivities; thus, more recently solid membrane electrodes have been prepared using various polymer matrix materials. For calcium ion-selective electrodes, polyvinyl acetate or polyvinyl chloride (PVC) matrix materials are used with organic phosphate ion exchanger (5). The need for the determination of many heavy metals in the environment has prompted the development of a number of neutral ionophores (6-9). To date much interest has been paid to the ionophore legands as sensing materials for neutral carrier type ion-selective electrodes (ISEs) due to the unique properties of the compounds.

The ionophores with oxygen donor atoms have been usually studied for many alkali and alkaline earth metal ISEs and many selective ligands have been found for these metal ions (10,11). Crown ethers are among the first synthetic complexing agents introduced to bind strongly and selectively to alkali metal ions (12).

Macrocyclic compounds such as porphyrin, cyclam, as well as crown ethers (13) are found to be neutracarrier ligands that complexes with lathanides and many heavy metal ions (14) to form ionophores that are sensitive and selective for these ions.

In a study, a polymeric membrane doped with gallium metalloporphyrin was prepared and was found selective to  $(\text{F}^{-})$  ions (15). In another study, a supported liquid membrane containing diisostearyl phosphoric acid was used indirectly to separate  $\text{In}^{3+}$  and  $\text{Ga}^{3+}$  (16). Since there are no investigations about gallium membrane electrodes prepared using crown ethers as neutral carriers; the aim of this study was to construct, characterize and use some of them in potentiometric determination of gallium ions. These electrodes were prepared using crown ethers such as 12-crown-4, benzo-15-crown-5 as active material and DOPP, DBP, DBPH as plasticizers in PVC matrix. Their optimum working conditions for the determination of gallium were investigated. Interference studies have been made and

these electrodes have been used for the determination of gallium ions using direct, standard addition and potentiometric titration methods.

### Experimental Part

**Apparatus and Equipment:** For the potentiometric measurements an Orion model EA940 expandable ion analyzer was used. A pH-meter model PHM-82 Radiometer Copenhagen and a combined glass electrode type Orion 91-02 Swiss made were used for pH measurements.

A calomel electrode Gallenkampe type was used as the outer reference electrode.

As the inner reference, a home-made Ag/AgCl electrode was prepared.

**Reagents and Solutions:** All reagents and chemicals used in this study were of analytical grade obtained from different companies.

Deionized double-distilled water was used for the preparation of solutions and throughout the experimental work.

Crown compounds 12-crown-4 (12C4), and benzo-15-crown-5 (B15C5) were obtained from Fluka company. Plasticizers dioctyl phenyl phosphonate (DOPP), dibutyl phosphate (DBP) and dibutyl phthalate (DBPH) were obtained from Aldrich and Fluka companies.

Stock solution of 0.1M gallium chloride was prepared in deionized water acidified with HCl.

Stock solutions of 0.1M LiCl, MgCl<sub>2</sub>, ZnCl<sub>2</sub>, AlCl<sub>3</sub>, Cr (NO<sub>3</sub>)<sub>3</sub> were also prepared.

The other standard solutions were prepared by dilution.

#### Preparation of gallium picrate complexes with crown ethers:

Following the procedures given in reference (17) for preparation of gallium picrate and its complex with crown ether, 10 mmole of Ga<sub>2</sub>O<sub>3</sub> was added to 25 ml aqueous solution containing 80 mmole picric acid and heating the mixture at 80°C with stirring for about 40 minutes. The aqueous solution was evaporated slowly after removing the excess acid with benzene. The yield was yellow crystals of Ga (Pic)<sub>3</sub>. 1 mmole of this gallium picrate was then dissolved in 10 ml of acetone and added to 15 ml of acetone containing B15C5. The

mixture was refluxed at 60°C for about 40 minutes, a yellow precipitate was obtained after cooling and drying. Another complex was prepared similarly using 12C4.

**Assembly of the electrode:** Construction of the electrode body and the immobilization of crown ether complexes in PVC matrix membrane was done using the method given by Craggs et. al. (18). The glass tube was  $\frac{3}{4}$  filled with 0.01M GaCl<sub>3</sub> solution before fixing the socket. The membrane was immersed in a standard solution 0.1M of the same ion for about 24 hours before using it for measurements.

**Electrode response and selectivity:** The potentials for a series of standard solutions ( $10^{-6}$  M –  $10^{-1}$  M) Ga<sup>3+</sup> was measured at different pH ranged from 1 – 12 (The pH value were adjusted with dilute NH<sub>4</sub>OH and HCl) using a potentiometric cell equipped with a magnetic stirrer.

A calibration curve was constructed for each electrode. The curves were plotted on Orion 7 cycle semi-logarithmic graph paper.

Using the mixed solutions method (19), the selectivity of each electrode was evaluated by mixing a fixed concentration of the analyte (0.0M,  $10^{-3}$ M,  $10^{-4}$ M) with different concentrations of one of the interfering ions: Li<sup>1+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup>, Al<sup>3+</sup>, Cr<sup>3+</sup> and measuring the potential of each mixture.

**Sample analysis:** The concentrations of three prepared synthetic samples ( $10^{-3}$  M,  $5 \times 10^{-4}$  M,  $10^{-4}$  M) Ga (III) ions were measured using direct, standard addition and titration methods.

In the standard addition method, a relatively high concentration of Ga<sup>3+</sup> solution was added in small portions (0.2ml.) to the sample solution and the potential was measured before and after each addition. A plot of antilog E/S versus the volume of the added standard was obtained for each sample.

In the titration method 100 mL of sample solution was titrated with  $10^{-2}$  M potassium hydroxide. A Gran's plot paper (semi antilogarithmic paper) was used to plot the electrode potential versus the volume of titrant (20).

## Results and discussion

In this work, six sensors have been prepared based on PVC membranes using Ga (III) picrate complexes with 12-crown-4 and benzo-15-crown-5 dissolved in different plasticizers. The parameters for these electrodes including slope, detection limit, linear range, correlation coefficient ( $r$ ) and life time were listed in table (1).

The calibration curves for Ga-selective electrodes based on 12C5 and B15C5 as sensors and DBPH as a plasticizers gave an excellent linear range (table 1), although the Ga-electrode based on 12C4 and DBPH has a wider linear range than that using B15C5 and DBPH. This is due to the compatibility between the components of the membrane. Figure (1) shows the calibration curves of the Ga-electrodes based on crown ethers DBPH as a plasticizer.

The results of the electrodes parameters show that the electrode based on 12C4 and DBPH as a plasticizer gives a response for gallium ions better than the response given by electrode based on B15C5 and DBPH, where the slope was 20.0 mV / decade with a detection limit of  $4 \times 10^{-6}$  M.

The gallium electrodes based on membranes that use DOPP as a plasticizer have good linearity (table 1) with slopes (20.4, 19.3) mV/decade for membranes nos. 3,4. From the results obtained, the electrode based on 12C4 and DOPP as a plasticizer is considered more sensitive than the electrode using B15C5 and DOPP because of its higher slope value (20.4 mV / decade) and lower detection limit ( $7 \times 10^{-6}$  M) compared with the slope value of the electrode no.4 (19.3 mV/decade) and detection limit ( $2.7 \times 10^{-5}$  M). This is due to the compatibility between the active material and the plasticizer.

The investigation was carried out for electrodes using DBP as a plasticizer. The calibration curves for electrodes using DBP have shown a shorter linear range (table 1) than the other constructed Ga-electrodes in range between  $8.0 \times 10^{-5}$  M to  $1.0 \times 10^{-2}$  M with slope values (24.1, 18.7) mV/decade which are far from the Nernstian slope value for the trivalent ions (19.7 mV/decade). However, the electrode based on 12C4 and DBP show a sensitive response due to its high slope value (24.1 mV/decade).

The response time for Ga-electrodes were generally found to range from 30 seconds to 6 minutes. The electrode based on B15C5 and DBPH as a plasticizer have attained a steady response time after 30 seconds and 70 seconds for solutions  $1.0 \times 10^{-1}$  M and  $1.0 \times 10^{-5}$  M respectively. The electrode with 12C4 and DBPH as a plasticizer was found to reach equilibrium after 50 seconds and 90 seconds for solutions  $1.0 \times 10^{-1}$  M and  $1.0 \times 10^{-5}$  M, respectively. These differences in the response times may be attributed to the large cavity size of ligand B15C5 with respect to the ionic radius of  $Ga^{3+}$  which facilitate the adaptation and cause quick release of  $Ga^{3+}$ . For electrodes based on DOPP, the response time is ranged from 70 seconds to 120 seconds which is nearly similar to those based on DBPH. This may be due to that the two plasticizers have comparable viscosities (16.7 cST for DOPP and 14.44 cST for DBPH) while the response times for Ga-electrodes using DBP as a plasticizer were relatively long where it was ranged from 2 minutes to 6 minutes for solutions  $1.0 \times 10^{-1}$  M to  $1.0 \times 10^{-5}$  M, respectively. This may be attributed to the high viscosity of DBP (112.884 cST) which lowers the mobility of the complex inside the membrane.

Electrodes based on 12C4 with DOPP and DBPH could be used for about 1.5 months to 2 months without observing any deviation while membranes based on B15C5 with the same plasticizers have life times less than one month. This change in life times is due to the leaching of the complex from the membrane to the external solution (21). The life times for electrodes using DBP were also less than one month which is due to incompatibility between the components of the membrane which made them leach out of the membrane.

The effect of pH on the electrode response was also investigated, where the working pH range for the Ga-electrodes using different crown ethers and different plasticizers was determined and listed in table (1). Above these pH values responses gradually deviate from the normal values. This may be due to the formation of  $Ga(OH)_3$  which has found a limitation for determination of gallium by other analytical methods. Figure (2) shows the typical pH effect for membranes nos. (1) and (3).

Interferences of  $Li^+$ ,  $Mg^{2+}$ ,  $Zn^{2+}$ ,  $Al^{3+}$  and  $Cr^{3+}$  on the electrode response were investigated. A mixed solution method was used, the potential for a series of standard solutions containing a fixed concentration of gallium ions with different concentrations of the

interfering ion were measured for Ga-electrodes based on 12C4 and B15C5 using DBPH as a plasticizer. The ratios of interfering ions are listed in table (2) for each ion with respect to each electrode.

From the results, it was found that the electrode based on 12C4 showed a selectivity better than the selectivity showed by the electrode based on B15C5 for Ga (III) over the  $\text{Cr}^{3+}$ . The variation in ratio for mono-di-and tri-valent ions is due to cation-cavity size

relationship, assuming the ionophore adopt a cavity-like structure at the event of complexation with the metal ion.

**Sample analysis:** Three synthetic samples of Ga (III) ions were prepared and their concentrations were determined using Ga-electrode based on 12C4 and DBPH as a plasticizer by direct, standard addition and titration methods.

Good results were obtained using direct method, where the RE% did not exceed 3.09% and the RSD% not more than 2.83%.

In standard addition method (22), the plot of antilog E/S versus the volume of the multiple addition of the standard was used to determine the concentration of Ga (III) ions in the synthetic samples. A typical plot is shown in figure (3).

In the titration method, a plot was constructed using Gran's plot paper (23). The samples were titrated against 0.01M potassium hydroxide solution. A typical Gran's plot is shown in figure (4).

All methods show comparable results with each other and with the theoretical concentrations as illustrated in table (3).

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Table (1) properties and working pH range of gallium selective electrodes using direct crown compounds and plasticizers

Electrode No.	Crown ether	Plasticizer	Slope mV/decade	Detection Limit/M	Conc. Linear Range/M	Correlation Coefficient (r)	Life Time (day)	pH-range
1	12C4	DBPH	20.0	$7.0 \times 10^{-6}$	$1.0 \times 10^{-5}$ – $3.3 \times 10^{-2}$	0.9998	57	3.0-5.0
2	B15C5	DBPH	19.3	$1.0 \times 10^{-5}$	$3.7 \times 10^{-5}$ – $1.0 \times 10^{-2}$	0.9997	25	3.2-5.1
3	12C4	DOPP	20.4	$7.0 \times 10^{-6}$	$4.5 \times 10^{-5}$ – $1.0 \times 10^{-2}$	0.9998	49	2.8-4.7
4	B15C5	DOPP	19.3	$2.7 \times 10^{-5}$	$7.0 \times 10^{-5}$ – $2.8 \times 10^{-2}$	0.9989	22	2.9-4.8
5	12C4	DBP	24.1	$4.0 \times 10^{-5}$	$9.0 \times 10^{-5}$ – $2.0 \times 10^{-2}$	0.9994	23	3.3-5.0
6	B15C5	DBP	18.7	$3.2 \times 10^{-5}$	$8.0 \times 10^{-5}$ – $2.1 \times 10^{-2}$	0.9996	23	3.0-4.9

**Table (2) maximum allowable ratios of interfering ion to gallium ion ( $10^{-3}$  M) for gallium electrodes using DBP/II plasticizer**

Crown Ether Compound	Maximum Ratio Interference				
	Li <sup>1+</sup>	Mg <sup>2+</sup>	Zn <sup>2+</sup>	Al <sup>3+</sup>	Cr <sup>3+</sup>
12C4	77	64	69	21	24
B15C5	75	55	60	19	20

**Table (3) gallium ion sample analysis using gallium electrode (membrane no. 1)**

Calculated Conc./M	Measured Concentration/M			
	direct	Standard Addition	Multiple standard Addition	Titration
$1.0 \times 10^{-3}$	$9.923 \times 10^{-4}$	$9.947 \times 10^{-4}$	$9.993 \times 10^{-4}$	$9.017 \times 10^{-3}$
RSD%	1.078	1.668	0.921	0.983
RE%	0.77	0.53	0.07	1.7
$5.0 \times 10^{-4}$	$4.948 \times 10^{-4}$	$4.973 \times 10^{-4}$	$5.008 \times 10^{-4}$	$4.966 \times 10^{-4}$
RSD%	2.829	2.674	2.196	1.309
RE%	0.52	0.54	0.16	0.68
$1.0 \times 10^{-4}$	$9.691 \times 10^{-5}$	$9.720 \times 10^{-5}$	$1.011 \times 10^{-4}$	$0.970 \times 10^{-4}$
RSD%	0.918	1.337	1.483	2.268
RE%	3.09	2.8	1.1	3.0

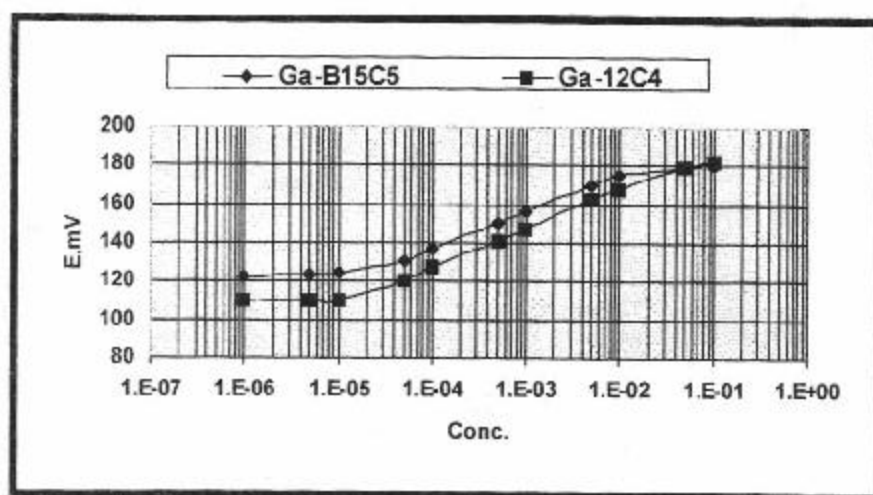


Fig. (1) Calibration curves of gallium electrodes based on crown ethers and DBPH plasticizer

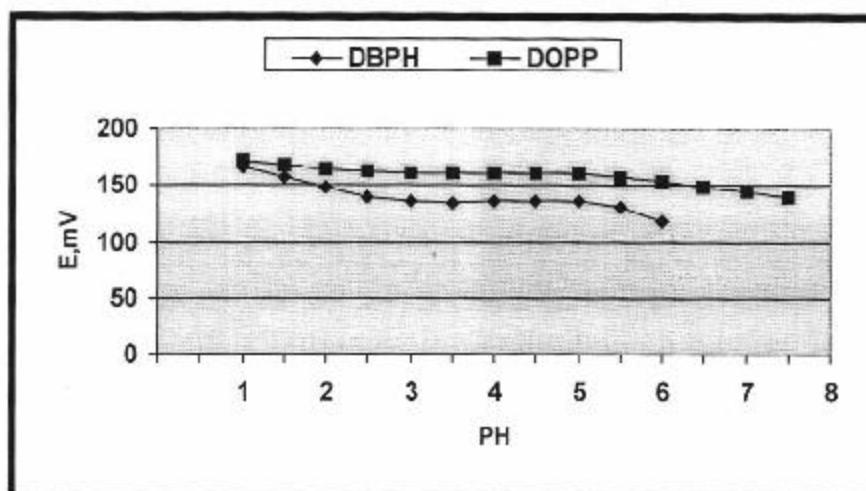


Fig. (2) pH effect on potential response for gallium electrode based on 12C4 (membrane no. 1,3)

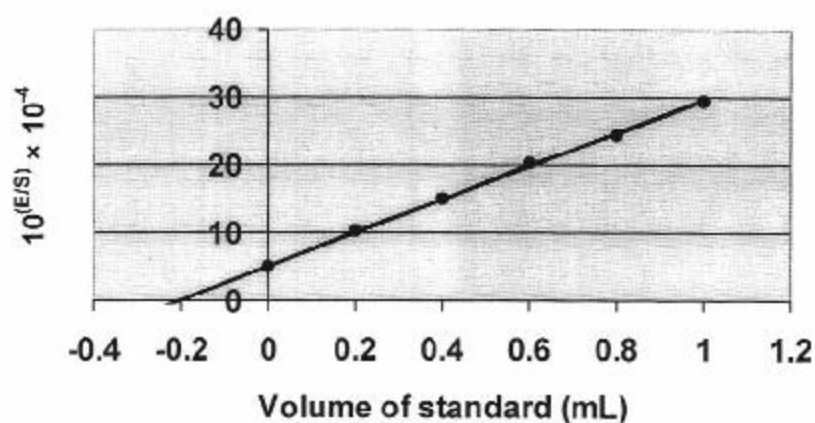


Fig. (3) Determination of gallium in sample solution  $10^{-3}$  M by multiple standard addition method

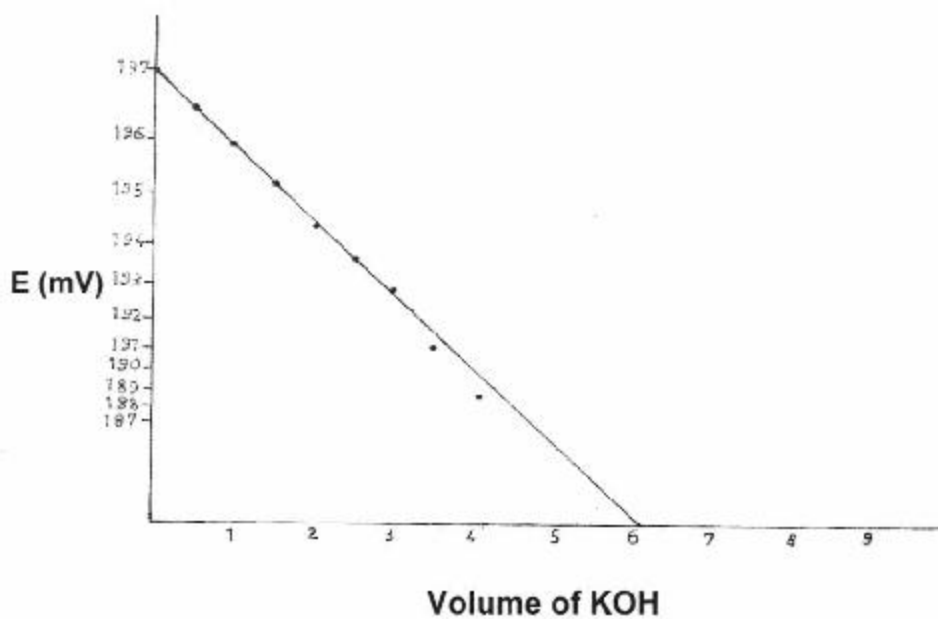


Fig. (4) Gran's plot for the titration of gallium in sample solution ( $10^{-3}$  M) against  $10^{-1}$  M KOH

## أقطاب الكاليوم الغشائية البوليمرية الانتقائية المعتمدة على الأيثرات التاجية

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### الخلاصة

تم تصنيع أقطاب غشائية بوليمرية إنتقائية للكاليوم مع المركبين التاجيين 12- (12C4) و crown-4 و benzo-15-crown-5 (B15C5) وباستخدام المواد الملدنة (DOPP) dioctyl phthalate و (DBPH) dibutyl phthalate، (DBP) dibutyl phosphate، phenyl phosphonate وبوجود مادة PVC .

درست مواصفات هذه الأقطاب والتي شملت الإستجابة والإنحدار، حد التحسس، مديات التراكيز، زمن الإستجابة وعمر القطب، فضلاً عن تأثير الدالة الحامضية، كما درست إنتقائية هذه الأقطاب بوجود أيونات مثل  $Li^+$ ،  $Mg^{2+}$ ،  $Zn^{2+}$ ،  $Al^{3+}$ ،  $Cr^{3+}$  كمتداخلات.

أظهر قطب الكاليوم البوليمري السائل المعتمد على الإيثر التاجي 12C4 والمادة الملدنة DBPH أفضل النتائج نسبة إلى أقطاب الكاليوم المحضرة الأخرى في مدى من الدالة الحامضية تراوح بين 3 - 5 ولمدى واسع من التراكيز تراوح بين  $1.0 \times 10^{-5}$  -  $3.3 \times 10^{-2}$  مولاري وإنحدار نرنستي 20 decade/mV وزمن إستجابة قصير وحد تحسس  $7 \times 10^{-6}$  مولاري وعمر زمني بحدود شهرين. كما أظهر القطب إنتقائية جيدة لأيونات الكاليوم بوجود أيونات أخرى. أستعمل قطب الكاليوم كقطب دليل في التسحيحات الجهدية لتقدير أيونات الكاليوم في المحاليل.