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The use of crown ethers as sensor material in potentiometry technique

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Abstract: Potentiometric methods are a type of electrochemical analysis which are used widely in many applications due to their multiple advantages such as wide concentration range, low detection limit, high selectivity, and sensitivity. Potentiometric sensors have many advantages over the other analytical methods and have been successfully applied in different real sample analyzes. Crown ethers are a group of macrocyclic compounds and have been used as ionophores by researchers due to their favorable chemical structures. In this review, we provide a description on crown ethers used as ionophores in potentiometric sensors.

Keywords: Crown ether; ion–selective electrode; potentiometry; ionophore; sensor.

1. Introduction

Synthesis of crown ether compounds is important in organic and supramolecular chemistry.[1] The first synthetic method was reported by Charles Pedersen in 1967 (Figure 1).[2,3] Crown ethers contain multiple $–CH_2CH_2O–$ units, which are connected to form a circular molecule.[4] They have advantages of high resistance to chemicals, temperature, radiolysis, and polar solvents.[5] One of their most important features is that they can make complexes with a wide variety of cations in the empty cavity center in the center of the ring (Figure 2).[6,7] They have attracted attention as their unique capability to form host–guest (1:1) complexes with cations.[8] The stability of the host–guest complex depends on the number of crown ether donor atoms.[9] They have been used in many fields, including chemical sensors, organic synthesis, chromatographic techniques, and phase transfer catalysts.[10] In addition, they are known to exhibit various biological activities such as antimicrobial,[11] antiproliferative,[12] antifungal,[13] anti-inflammatory[14] and antimutagenic.[15]

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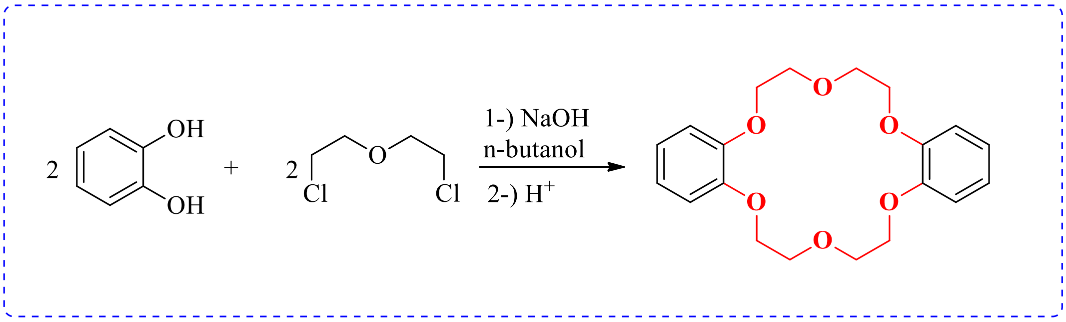


Figure 1. Pedersen's synthesis of first crown ether

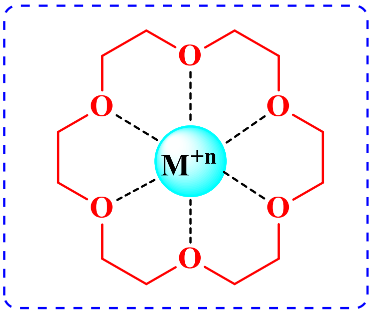


Figure 2. The metal complex of the crown ethers

Potentiometric methods are highly important in the field of electroanalytical chemistry and commonly used for the determination of different ions.[16,17] Potentiometric ion–selective electrodes offer important advantages including wide concentration range, low detection limit, long lifetime, low cost, ease of use, high selectivity and sensitivity and short response time etc.[18–22] Because of these advantages, potentiometric sensors are widely used in areas such as environmental monitoring, industrial, agricultural and drug analysis.[23,24] A significant number of crown ether derivatives have been used in the construction of potentiometric sensors to determine different metal cations in real samples.

Ionophore, the most important component of potentiometric ion–selective electrodes (ISEs) is responsible for the selective response to a target ion.[25,26] Macrocyclic compounds, including porphyrins, crown ethers and calixarenes are often used as materials in potentiometry–based sensors due to their sensitivity and selectivity toward various ions.

2. Crown–Ether Based Potentiometric Sensors

Crown ether–based potentiometric sensors have shown significant sensitivity to many different cations. Gupta *et al*. developed an aluminum(III)–selective potentiometric electrode using 12-crown-4 **(1)** (Figure 3) as ionophore.[27] This aluminum(III)–selective electrode in the linear range of 1.0×10^{-6} – 1.0×10^{-1} M, did not affect the changes in pH between 2.0–7.8. In addition, the developed electrode was applied for the analysis of aluminum(III) in andesite, basalt, rhyolite, granite, and Al-Mg syrup, and results were given in comparison to atomic emission spectrometry (AES). Another work, where a 12-crown-4 **(1)** molecule was used as an ionophore in the structure of zinc(II)–selective sensor, was proposed by Gupta.[28] The proposed potentiometric sensor had a wide concentration range of 7.0×10^{-5} – 1.0×10^{-1} M against Zn^{2+} ions and a response time of less than 10 s. Kumar *et al.* reported a copper(II)–selective potentiometric sensor using the same ionophore **(1)**.[29] The developed sensor worked in a concentration range of 1.78×10^{-5} – 1.0×10^{-1} M and had a response time of <30s.

Khaled *et al.* developed a disposable screen–printed lead(II)–selective potentiometric sensor using 15-crown-5 **(2)** (Figure 3) as an ionophore.[30] They reported that this sensor worked in the linear concentration range of 1.0×10^{-6} – 1.0×10^{-2} M and had a lower detection limit of 2.0×10^{-7} M. This lead(II)–selective sensor had a response time of <2 s, and was successfully applied to the determination of Pb^{2+} ions in environmental samples. Another potentiometry–based sensor developed by Karimian *et al.* was a silver(I)–selective sensor prepared by using 15-crown-5 **(2)** as an ionophore,[31] which was reported to have a wide working concentration range of $1.0 \times 10^{-7} - 1.0 \times 10^{-1}$ M. It had a lifetime of 2 months and a response time of approximately 10 s. The proposed sensor was successfully used in the determination of Ag^{+} ions in radiology wastes. They compared the results of the sensor (2.77 ± 0.04 mmol L^{-1}) with atomic absorption spectrometry (AAS) (2.65 ± 0.02 mmol L^{-1}), and reported to be in a good agreement.

A study on lead(II)–selective coated graphite potentiometric electrode using a benzo-18-crown-6 **(3)** was performed by Ghorbani *et al*.[32] The sensor had a Nernstian slope of 28.80 mV/decade and a pH working range of 1.5 to 5.0. Ekmekci *et al*. developed an iron(III)–selective potentiometric electrode with the same ionophore **(3)** (Figure 3).[33] The electrode worked in a wide concentration range of $1.0 \times 10^{-6} - 1.0 \times 10^{-1}$ M, and was successfully applied in blood and grape molasses. Ganjali *et al.* reported a poly(vinly chloride) (PVC) membrane beryllium selective sensor using napto-9-crown-3 **(4)** (Figure 3) as an ionophore.[34] The beryllium selective sensor showed a wide concentration range of $8.0 \times 10^{-6} - 1.0 \times 10^{-1}$ M with a detection limit of 6.0×10^{-6} M. In addition, this sensor was successfully applied to the determination of Be^{2+} ions in binary mixtures. Govindan *et al*. reported a potentiometric lithium–selective electrode using 6,6-dibenzyl-14-crown-4 **(5)** (Figure 3) as an ionophore.[35] The electrode was successfully applied to the determination of lithium ions in complex chemical matrices.

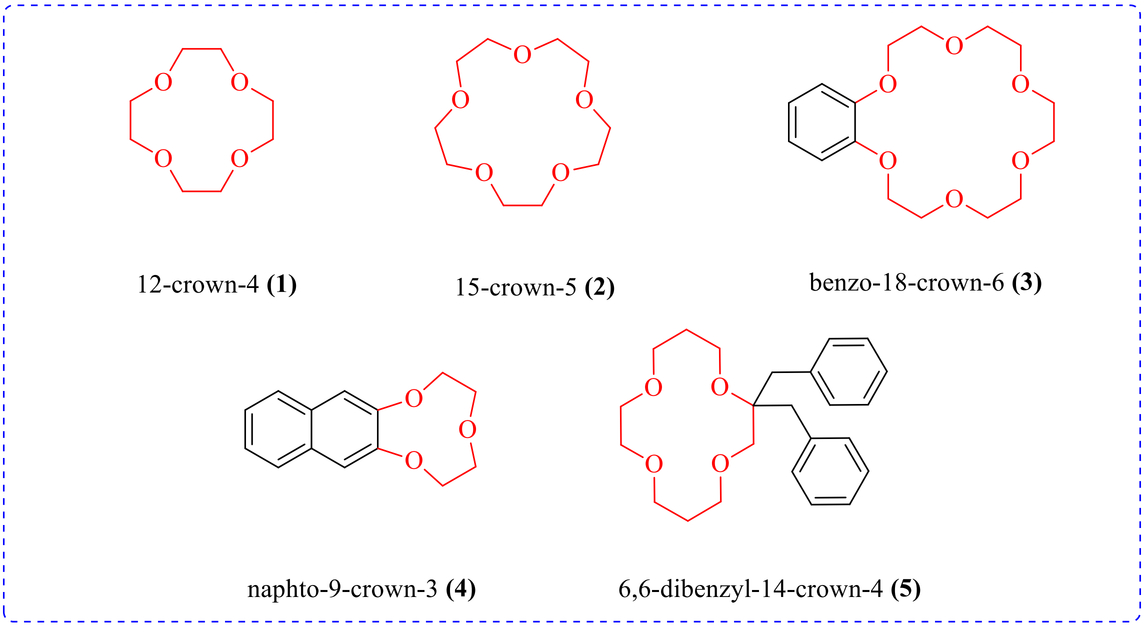
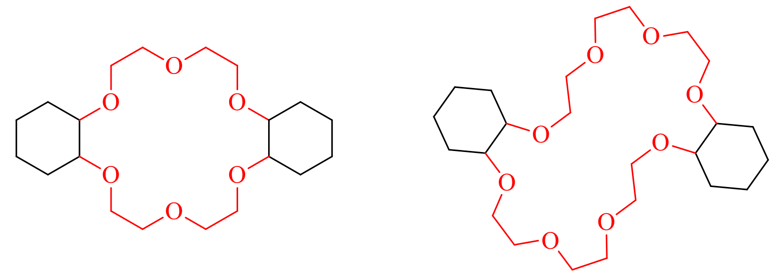


Figure 3. Crown ethers **1**, **2**, **3**, **4** and **5** used as ionophores

Gupta and coworkers used dicyclohexano-18-crown-6 **(6)** (Figure 4) as an ionophore to fabricate a cadmium(II)–selective sensor,[36] which worked at a concentration fange of $2.1 \times 10^{-5} - 1.0 \times 10^{-1}$ M and had a Nernstian slope of 29.0 ± 1.0 mV/decade. The proposed sensor was applied in wastewater samples. Mittal *et al*. used the same molecule **(6)** (Figure 4) as an ionophore in the lanthanum(III)–selective sensor.[37] The sensor was reported to have a working range of $1.0 \times 10^{-6} - 1.0 \times 10^{-1}$ M and had a low detection limit (5.0×10^{-7} M). In addition, the lanthanum(III)–selective sensor was not affected by the change of pH in the range of 4.0–9.0.

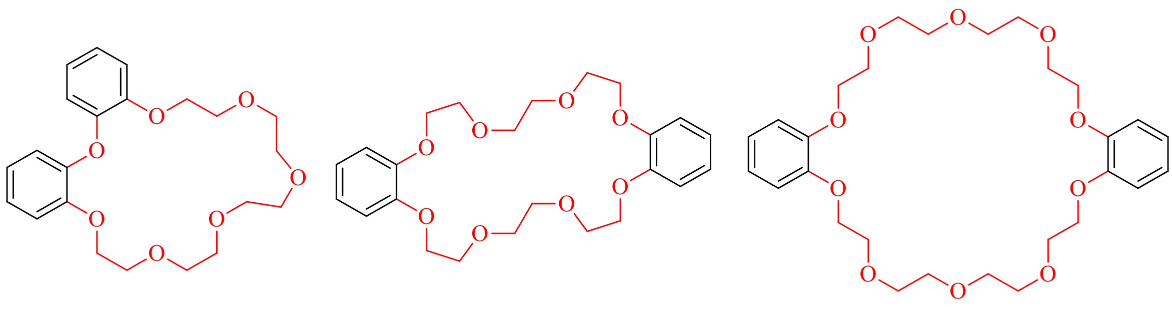
PVC membrane cadmium(II)–selective sensor was developed by Gupta *et al*. using dicyclohexano-24-crown-8 (Figure 4) **(7)** as an ionophore.[38] This sensor had a working range of $3.0 \times 10^{-5} - 1.0 \times 10^{-1}$ M and exhibited Nernstian behavior (30.0 ± 1.0 mV/decade). Tin(II)–selective PVC membrane sensor was proposed by Aghaie *et al*.[39] They used dibenzo-18-crown-6 **(8)** (Figure 4) as an ionophore, having a linear working range of $1.0 \times 10^{-6} - 1.0 \times 10^{-2}$ M and a lower detection limit of 8.0×10^{-7} M. In addition, the sensor was used in determination of Sn^{2+} in various spiked samples. Akl and Abd El-Aziz developed a PVC membrane zinc(II)–selective sensor using 18-crown-6 and dibenzo18-crown-6 **(8)** molecules as ionophores.[40] The proposed sensors had concentration ranges of $1.0 \times 10^{-5} - 1.0 \times 10^{-1}$ M. The zinc(II)–selective sensors were used for the determination of zinc in alloy samples. Additionally, the data of zinc(II)–selective sensors were compared with AAS data. They reported that the results of the two methods were consistent. Gupta *et al*. used dibenzo-18-crown-6 **(8)** as an ionophore and proposed a nickel(II)–selective potentiometric sensor,[41] working in a wide concentration range of $1.0 \times 10^{-5} - 1.0 \times 10^{-1}$ M. The sensor had a response time of approximately 25 s and was successfully used to determine Ni^{2+} ions in Indian brand chocolates.



dicyclohexano-18-crown-6 **(6)** dicyclohexano-24-crown-8 **(7)** dibenzo-18-crown-6 **(8)**

Figure 4. Crown ethers **6**, **7** and **8** used as ionophores

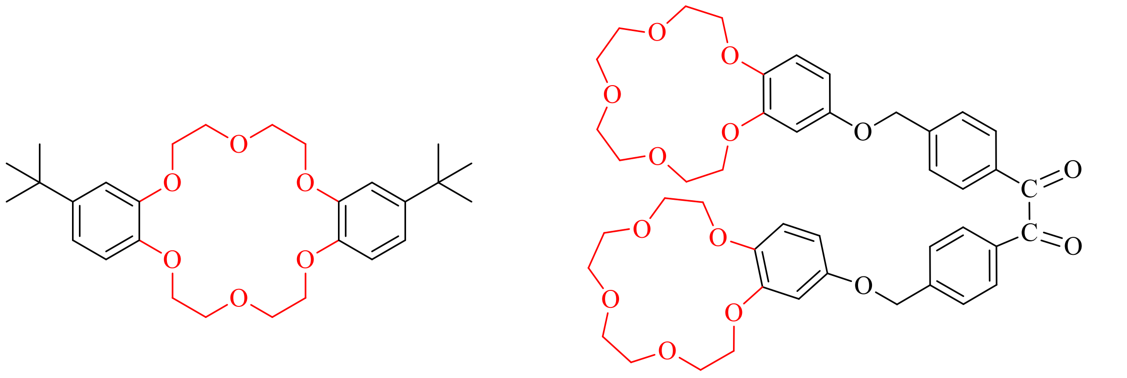
Shamsipur *et al*. developed a potentiometric sensor using dibenzo-21-crown-7 **(9)** (Figure 5) as an ionophore to determine Rubidium ions in tap water samples,[42] which showed a linear response in the concentration range of $5.0 \times 10^{-5} - 1.0 \times 10^{-1}$ M and a pH range of 3.5–8.0. Potentiometric determination of cadmium(II) ions was performed by Gupta and Kumar using dibenzo-24-crown-8 **(10)** (Figure 5) as an ionophore.[43] This sensor displayed a linear response in a concentration range of $3.9 \times 10^{-6} - 1.0 \times 10^{-4}$ M and had a Nernstian slope of 30.0 ± 1.0 mV/decade. They also stated that the sensor had good selectivity and reproducibility. Another sensor based on dibenzo-24-crown-8 **(10)** as an ionophore was reported by Gupta *et al*. for the potentiometric determination of Zn^{2+} ions.[44] The sensor had a concentration range of $9.2 \times 10^{-5} - 1.0 \times 10^{-1}$ M. It had a pH working range from 4.8 to 6.2 and a response time of 12 s. In addition, the developed sensor was successfully applied to the determination of Zn^{2+} ions in wastewater samples. Ganjali *et al*. developed a potentiometric sensor to determine strontium(II) ions in synthetic water samples.[45] They used dibenzo-30-crown-10 **(11)** (Figure 5) as an ionophore. This sensor worked in the concentration range of $1.0 \times 10^{-5} - 1.0 \times 10^{-2}$ M and was shown to be usable in the pH range of 3.0–10.0.



dibenzo-21-crown-7 **(9)** dibenzo-24-crown-8 **(10)** dibenzo-30-crown-10 **(11)**

Figure 5. The crown ethers used as ionophores (**9**, **10** and **11**)

Sadeghi and Fathi prepared a cesium ion–selective sensor, using 4',4",(5')di-tert-butyldibenzo-18-crown-6 **(12)** (Figure 6) as an ionophore.[46] The sensor was shown to work in the concentration range of $6.0 \times 10^{-6} - 1.0 \times 10^{-2}$ M and to have a detection limit of 4.0×10^{-6} M. The sensor was used in determination of Cs^{+} in spiked tap water samples. The potassium(I)–selective potentiometric sensor was developed by Kemer and Ozdemir.[47] They used 4,4'-bis[4"-phenoxy(15-crown-5)methyl]benzyl molecule **(13)** (Figure 6) as an ionophore, which had a linear working range of $1.0 \times 10^{-5} - 1.0 \times 10^{-1}$ M and a lower detection limit of 1.0×10^{-7} M. Additionally, this sensor was successfully applied in different water samples.

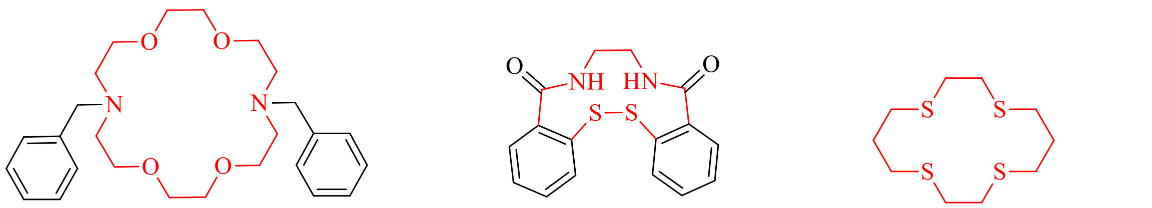


4',4",(5')di-tert-butyldibenzo-18-crown-6 **(12)** 4,4'-bis[4"-phenoxy(15-crown-5) methyl]benzyl **(13)**

Figure 6. The crown ethers **12** and **13** used as ionophores

Isildak *et al*. reported *N*,*N'*-dibenzyl-4,13-diaza-18-crown-6 **(14)** (Figure 7) as an ionophore in design of PVC membrane zinc(II)–selective sensor.[48] The proposed sensor worked in a wide concentration range of $1.0 \times 10^{-5} - 1.0 \times 10^{-1}$ M and exhibited a Nernstian behavior (28.0 ± 2.0 mV/decade). In addition, the sensor had a fast response time of 5 s. Finally, zinc(II)–selective sensor was successfully applied to the potentiometric determination of zinc(II) ions in different water samples and a drug sample. Another work, where *N*,*N'*-dibenzyl-4,13-diaza-18-crown-6 **(14)** molecule was used as an ionophore. The lead(II)–selective PVC membrane potentiometric sensor was reorted by Gupta *et al*,[49] which had a linear working range of $8.2 \times 10^{-6} - 1.0 \times 10^{-1}$ M with a Nernstian slope of 30.0 ± 2.0 mV/decade. The proposed sensor exhibited a fast response time of about 10 s and a pH working range of 2.0–6.8.

A silver(I)–selective polymeric membrane sensor, based on dilaktam crown ether **(15)** (Figure 7), was developed by Masrournia *et al*.[50] It exhibited a working concentration range of $1.0 \times 10^{-5} - 1.0 \times 10^{-1}$ M and a low detection limit of 6.8×10^{-6} M. The electrode was successfully used as an indicator electrode in the potentiometric titration of Ag^+ against NaCl. A lead(II)–selective PVC membrane sensor based on 1,4,8,11-tetrathiacyclotetradecane **(16)** (Figure 7) was reported by Elmosallamy *et al*,[51] having a concentration range of $1.0 \times 10^{-5} - 1.0 \times 10^{-2}$ M with a Nernstian slope of 29.9 mV/decade. It was successfully used in the determination of Pb^{2+} ion in the some alloy samples.



N,*N'*-Dibenzyl-4,13-diaza-18-crown-6 **(14)** dilaktam crown ether **(15)** 1,4,8,11-tetrathiacyclotetradecane **(16)**

Figure 7. The crown ethers used as ionophores

Golcs *et al.* developed lead(II)–selective sensors by using acridono-crown ethers (**17** and **18**) (Figure 8) as ionophores.[52] They exhibited a Nernstian response for lead(II) ions in the concentration range of $1.0 \times 10^{-4} - 1.0 \times 10^{-2}$ M. Furthermore, they reported the use of these lead(II)–selective sensors in the analysis of multicomponent aqueous samples.

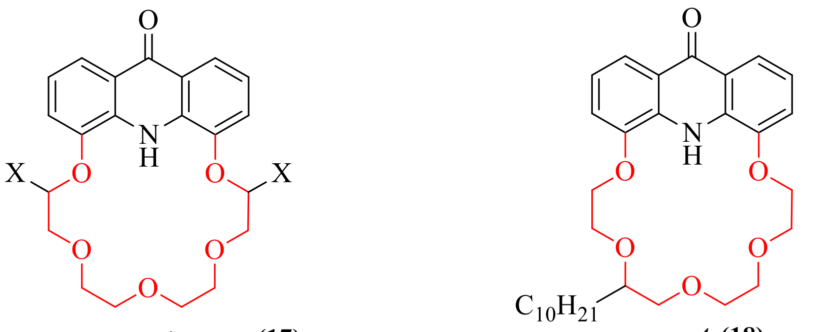


Figure 8. The acridono–crown ethers used as ionophores

Potentiometric characteristics and membrane components of the crown ether–based potentiometric sensors available in the literature are given in Tables 1 and 2. The ionophore (crown ether derivative) ratio in the prepared sensors varies between 0.5 and 9.0% (Table 1). Besides, it is noteworthy that all the reported sensors have PVC membrane structures.

Table 1. Membrane components of crown ether–based potentiometric sensors in the literature

Composition (%, *w/w*)				
Ionophore	**Additive**	**Plasticizer**	**PVC**	**Ref.**
3.0	6.5 (OA)	61.5 (DBP)	29.0	27
4.5	4.5 (NaTPB)	45.5 (DOP)	45.5	28
4.5	–	4.5 (DBF)	90.9	29
0.58	0.17 (NaTPB)	59.6 (*f*–PNPE)	39.7	30
5.6	3.9 (NaTPB)	60.5 (*o*–NPOE)	30.0	31
4.0	–	20.0 (DOP)	55.0	32
2.0	2.0 (TBATPB)	67.0 (NPPE)	29.0	33
9.0	3.0 (NaTPB)	58.0 (*o*–NPOE)	30.0	34
70.0 (ionophore, *o*–NPOE and KTpClPB)			30.0	35
6.2	1.2 (NaTPB)	46.3 (DBP)	46.3	36
6.0	–	61.0 (*o*–NPOE)	33.0	37
4.7	0.5	47.4 (DBBP)	47.4	38
5.0	5.0 (OA)	60.0 (AP)	30.0	39
1.1	–	65.9 (DOPP)	33.0	40
2.4	0.2	48.7 (TEHP)	48.7	41
6.5	2.7 (NaTPB)	56.9 (*o*–NPOE)	33.9	42
4.8	–	47.6 (DBBP)	47.6	43
3.2	0.64	32.0 (DOP)	64.1	44
5.0	10.0 (OA)	55.0 (BA)	30.0	45
8.0	1.0 (NaTPB)	58.0 (DOP)	33.0	46
4.0	1.0 (NaTPB)	55.0 (DOS)	40.0	47
4.0	1.0 (KTpClPB)	62.0 (BEHS)	33.0	48
3.83	0.32 (NaTPB)	31.9 (DBP)	63.9	49
4.0	–	63.0 (DOP)	33.0	50
1.0	–	66.0 (*o*–NPOE)	33.0	52

Table 2. Potentiometric characteristics of crown ethers–based potentiometric sensors

Ionophore	Ion	Concentration range (M)	Limit of detection (M)	pH working range	Response time (s)	Slope (mV/decade)	Life time (month)	Ref.
12-crown-4 **(1)**	Al^{3+}	1.0×10^{-6} – 1.0×10^{-1}	5.5×10^{-7}	2.0 – 7.8	15	–	2	27
12-crown-4 **(1)**	Zn^{2+}	7.0×10^{-5} – 1.0×10^{-1}	–	2.8 – 5.5	< 10	29.5 ± 1.0	3	28
12-crown-4 **(1)**	Cu^{2+}	1.78×10^{-5} – 1.0×10^{-1}	1.78×10^{-5}	3.0 – 6.0	< 30	50.0	6	29
15-crown-5 **(2)**	Pb^{2+}	1.0×10^{-6} – 1.0×10^{-2}	2.0×10^{-7}	–	< 2	31.14 ± 0.94	6	30
15-crown-5 **(2)**	Ag^{+}	1.0×10^{-7} – 1.0×10^{-1}	8.09×10^{-7}	3.0 – 8.0	< 10	58.9	2	31
benzo-18-crown-6 **(3)**	Pb^{2+}	1.0×10^{-5} – 1.0×10^{-1}	5.0×10^{-6}	1.5 – 5.0	30	28.8	3	32
benzo-18-crown-6 **(3)**	Fe^{3+}	1.0×10^{-6} – 1.0×10^{-1}	–	–	30	57.0 ± 1.0	2	33
naphto-9-crown-3 **(4)**	Be^{2+}	8.0×10^{-6} – 1.0×10^{-1}	6.0×10^{-6}	3.5 – 9.0	< 15	29.5	–	34
6,6-dibenzyl-14-crown-4 **(5)**	Li^{+}	1.0×10^{-4} – 2.0×10^{-1}	3.0×10^{-5}	4.0 – 8.0	< 100	58.5 ± 1.0	4	35
dicyclohexano-18-crown-6 **(6)**	Cd^{2+}	2.1×10^{-5} – 1.0×10^{-1}	–	1.9 – 7.0	17	29.0 ± 1.0	6	36
dicyclohexano-18-crown-6 **(6)**	La^{3+}	1.0×10^{-6} – 1.0×10^{-1}	5.0×10^{-7}	4.0 – 9.0	< 30	19.0	5	37
dicyclohexano-24-crown-8 **(7)**	Cd^{2+}	3.0×10^{-5} – 1.0×10^{-1}	–	2.0 – 5.4	23	30.0 ± 1.0	6	38
dibenzo-18-crown-6 **(8)**	Sn^{2+}	1.0×10^{-6} – 1.0×10^{-2}	8.0×10^{-7}	–	< 15	27.5 ± 0.6	3	39
dibenzo-18-crown-6 **(8)**	Zn^{2+}	1.0×10^{-5} – 1.0×10^{-1}	1.5×10^{-5}	4.0 – 8.0	< 15	30.0	2	40
dibenzo-18-crown-6 **(8)**	Ni^{2+}	1.0×10^{-5} – 1.0×10^{-1}	–	2.6 – 6.8	< 25	29.5	4	41
dibenzo-21-crown-7 **(9)**	Rb^{2+}	5.0×10^{-5} – 1.0×10^{-1}	1.5×10^{-6}	3.5 – 8.0	< 40	57.8	~2	42
dibenzo-24-crown-8 **(10)**	Cd^{2+}	3.9×10^{-6} – 1.0×10^{-1}	–	3.2 – 7.5	25	30.0 ± 1.0	5	43
dibenzo-24-crown-8 **(10)**	Zn^{2+}	9.2×10^{-5} – 1.0×10^{-1}	2.0×10^{-7}	4.8 – 6.2	12	29.0 ± 0.5	4	44
dibenzo-30-crown-10 **(11)**	Sr^{2+}	1.0×10^{-5} – 1.0×10^{-1}	5.0×10^{-6}	3.0 – 10.0	< 10	29.2 ± 0.3	4	45
4',4",(5')di-tert-butyldibenzo-18-crown-6 **(12)**	Cs^{+}	6.0×10^{-6} – 1.0×10^{-1}	4.0×10^{-6}	3.0 – 9.5	10	57.0 ± 1.8	3	46
4,4'-bis[4"-phenoxy (15-crown-5) methyl]benzyl **(13)**	K^{+}	1.0×10^{-5} – 1.5×10^{-1}	1.0×10^{-7}	5.0 – 7.0	< 10	55.0 ± 15	2	47
N,N'-Dibenzyl-4,13-diaza-18-crown-6 **(14)**	Zn^{2+}	1.0×10^{-5} – 1.0×10^{-1}	1.17×10^{-6}	4.0 – 11.0	5	28.0 ± 2.0	–	48
N,N'-Dibenzyl-4,13-diaza-18-crown-6 **(14)**	Pb^{2+}	8.2×10^{-6} – 1.0×10^{-1}	> 8.2×10^{-6}	2.0 – 6.8	10	30.0 ± 0.1	3	49
dilaktam crown ether **(15)**	Ag^{+}	1.0×10^{-5} – 1.0×10^{-1}	6.8×10^{-6}	5.1 – 7.2	20	59.8 ± 0.2	2.5	50
1,4,8,11-tetrathiacyclo tetradecane **(16)**	Pb^{2+}	1.0×10^{-5} – 1.0×10^{-2}	2.2×10^{-6}	3.0 – 6.5	20	29.9	3	51
acridono-crown ether (**17** and **18**)	Pb^{2+}	1.0×10^{-4} – 1.0×10^{-2}	7.9×10^{-6}	4.0 – 7.0	5	26.9	3	52

3. Applications of Crown Ether–Based Potentiometric Sensors

The real sample applications and recovery of PVC membrane crown ether-based potentiometric sensors reported in the literature are given in Table 3. The proposed crown ether–based sensors demonstrated very high recoveries in different real sample analyses. In addition, the developed potentiometric sensors showed compatible results with other analytical methods such as AAS, AES, pulse polargraphy and Inductively Coupled Plasma spectroscopy (ICP).

Table 3. Real sample applications of PVC membrane crown ether–based sensors in the literature

Ref.	Real Sample	Potentiometric Method	Other Analytical Method	
27	Andesite	4.09 ± 0.10 ppm		3.980 ± 0.005 ppm
	Basalt	3.62 ± 0.09 ppm		3.69 ± 0.08 ppm
	Rhyolite	4.61 ± 0.16 ppm	AES	4.98 ± 0.24 ppm
	Granite	3.21 ± 0.18 ppm		3.07 ± 0.23 ppm
	Al-Mg syrup	2.84 ± 0.20 ppm		2.85 ± 0.29 ppm
28	River water	4.6 mg dm^{-3}	AAS	4.5 mg dm^{-3}
			ICP	4.8 mg dm^{-3}
30	Tap water*	97.00 ± 1.25 %		
	River Nile water*	102.40 ± 0.98 %		
	Waste water*	104.20 ± 1.14 %		
31	Radiology wastes	2.77 ± 0.04 mmol/L	AAS	2.65 ± 0.02 mmol/L
33	Grape molasses	41.0 ± 5.0 μg/g	pulse polarg -raphy	49.0 ± 5.0 μg/g
39	Spiked samples	98.9 – 115.6 %		
40	Devarde’s Alloy samples	4.70 ppm	AAS	5.0 ppm
41	Chocolate samples	0.81 mg/kg	AAS	0.83 mg/kg
			ICP	0.84 mg/kg
42	Tap water*	95.6 – 102.8 %		
43	River water	2.3 mg dm^{-3}	AAS	2.2 mg dm^{-3}
			ICP	2.4 mg dm^{-3}
44	Battery waste	13.59 mg/L	AAS	13.62 mg/L
			ICP	13.63 mg/L
45	Binary and ternary* mixtures	99.8 – 103.1 %		
46	Spiked tap water	6.05 ± 0.10 μg/mL	AAS	6.25 ± 0.20 μg/mL
47	Tap water*	97.0 – 101.0 %		
48	Tap water*	94.0 %		
	Purification water*	97.75 %		
	Commercial water*	96.20 %		
	Drug sample	124.339 ppm	ICP	126.769 ppm
51	Alloy sample	2.1 ± 0.07 ppm	AAS	2.0 ± 0.05 ppm

*Standard addition method

Crown ethers were reported to be used as sensors in voltammetry technique (Table 4).

Table 4. Some crown–ether derivatives used in voltammetry technique

Crown ether	Ion	Concentration range	Limit of detection	Real sample	Ref
12-crown-4 **(1)**	Hg^{2+}	5.0 – 110.0 µg/ml	0.25 µg/ml	blood, urine, tap water	53
dicyclohexyl-18-crown-6	Tl^{+}	3.0 – 250.0 ng/mL	0.86 ng/mL	water and hair	54
benzo-15-crown-5	Cu^{2+}	1.0 – 100.0 ppb	0.05 ppm	alcoholic beverages	55
diaza-18-crown-6 **(14)**	Pb^{2+}	10.0 – 50.0 µg/L	0.09 µg/L	River water	56
18-crown-6	Hg^{2+}	1.0×10^{-5} – 6.0×10^{-6} M	2.0×10^{-7} M	Not reported	57

4. Conclusion

Macrocyclic molecules are used extensively by researchers in many fields due to their unique properties. These molecules, containing multiple donor atoms such as N, O, and S in their structures, can be considered sensor materials (ionophore) and exhibit selectivity towards various ions.[25] This review paper describes the use of crown ethers as ionophores in potentiometric ion-selective electrodes. Crown ethers, an important group of macrocycles, have been subject to extensive research in developing potentiometry–based sensors. They can bind to cations due to their structures with suitable cavities. Therefore, crown ethers are highly attractive molecules for sensor studies, and have been included as ionophores in many studies. As a conclusion, crown ethers are considered very attractive molecules as ion–selective electrodes.

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