

## One Decade of Research on Ion-Selective Electrodes in Iran (1996-2006)

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This review presents a general overview about the development of ion-selective electrodes in Iran during the past decade (1996-2006). All of the reported ion-selective sensors (for cations, anions and organic species) are cited in this review. Sensors for 39 cations, 12 anions, and 23 organic compounds and drugs have been reported in this review. Some of the main group cations (*e.g.* beryllium) as well as most of the lanthanide ion (*i.e.*, presidium, erbium, lutetium, cerium, neodymium, europium, gadolinium, terbium, dysprosium, holmium, ytterbium, and thulium) sensors have been reported for the first time. It is noticeable that the best reported sensors for  $\text{HPO}_4^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{ClO}_4^-$ ,  $\text{Br}^-$ , and  $\text{I}_3^-$  have been designed and constructed by the Iranian researchers.

**Keywords:** Sensors, Liquid membrane, Potentiometry, Ion-selective

## INTRODUCTION

### Liquid Membrane Sensor ISE

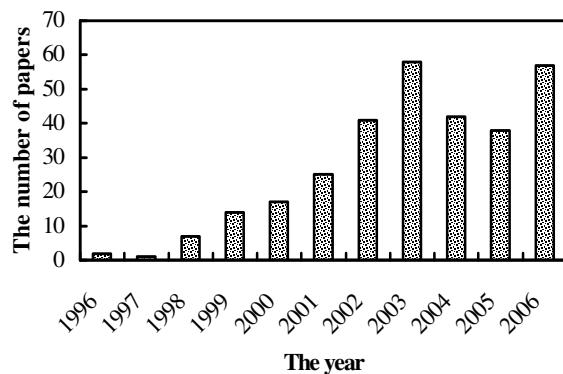
In general, a liquid membrane sensor is a device, comprising a non-polar solvent supported by a highly porous polymeric layer. The liquid membrane allows only the selective permeation of certain ionic species through itself, due to the incorporation of special ingredients, called "ionophore" or in other words "ion carrier". A consequence of this selective permeation is a potential difference formation at the two membrane surfaces, measured by the two reference electrodes at both sides of the membrane.

Despite the fact that other ingredients such as ionic additives, membrane solvent, and polymeric support can affect the membrane behavior. Knowing that the ion carrier is the most determining species in a liquid membrane ion selective electrode, the history of these devices and their design are going to be studied, with respect to the type of ionophores

used for their construction. The appearance order of the species in this article will be similar to the periodic table pattern.

## ION SELECTIVE ELECTRODES IN IRAN

In this review, we present the historical trend and status of



**Fig. 1.** Number of published papers vs. the year of publication.

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the studies performed on ion selective electrodes and their development during the last decade in Iran. Figure 1 depicts a statistical history of development of ion sensors in Iran over the past decade. The first sensors were developed in 1996 and 1997. At that time, the number of ion sensors reported by the Iranian researcher did not exceed the number of fingers in hands. Experiments on this field, however, caught on in the following years, increasing the average number of published reports to around 50 per year in recent years.

## CATION SELECTIVE SENSORS

Table 1 shows a summary of the cation-selective potentiometric sensors designed and constructed by the Iranian researchers over the past decade. This table contains the name of the ionophore, slope, linear range (LR), detection limits (DL),  $\log K_{\text{sel}}$  (selectivity coefficient), and type of the sensor (TS). Overall, there have been more than 190 reports on cation selective electrodes out of which about 60 of the sensors were selective for the main group metal ions.

In the field of alkali metal ions, the ionophores that have been used are mostly crown ethers and calixarens [1,2,4,5,7,8]. The ionophores were mostly used to construct PMEs (polymeric membrane electrodes) and CGEs (coated graphite electrodes), although a zeolite membrane electrode (ZME) was also reported as a  $\text{Cs}^+$  selective electrode [9]. The most common interfering ions in the case of first group metal were found to be  $\text{Pb}^{2+}$  and  $\text{NH}_4^+$ , in addition to the ions from the same group. The detection limits of these sensors were in the range of  $10^{-7}$ - $10^{-5}$  and almost all of the sensors revealed Nernstian or at least Very close-to-Nernstian calibration curve slopes [1-10]. The most sensitive alkaline metal sensors were two  $\text{K}^+$  polymeric membrane sensors based on 1,10-bis(2'-benzoic acid)-1,4,7,10-tetradecane and 1,7-bis(2'-benzoic acid)-1,4,7-trioxaheptane [3], which exhibited potential slopes of 61.8 and 62.6 mV dec<sup>-1</sup> of concentration, respectively.

As seen in Table 1, most of the alkaline earth metal ions were based on crown ether derivatives [11,13-18,24]. However other compounds like 3,4-di[2-(2-tetrahydro-2H-pyranoxy)] ethoxy styrene-styrene copolymer [12], 2,3,5,6,8,9-hexahydro-1,4,7,10-benzotetraoxacyclododecane-12-carbaldehyde-12-(2,4-dinitro-phenyl)hy [17], 1,13-diaza-3,4;12,13-dibenzo-5,8,11-trioxabicyclo[13.2.2]heptadecane-

2,14-dione [23], a synthesized benzo-9-crown-3 derivative [19], 1,4-diaza-2,3;8,9-dibenzo-7,10-dioxacyclododecane-5,12-dione [20], 2-[(2-hydroxyphenyl)imino]-1,2-diphenylethanone [21], dimethyl-1-(4-nitrobenzoyl)-8-oxo-2,8-dihydro-1H-pyrazolo[5,1-a] iso-indole-2,3-dicarboxylate [22], 1,13-diaza-2,3;11,12-dibenzo-4,7,10-trioxacyclopentadecane-14,15-dione [23] have also been reported to show selectivities to these ions. The sensors are mostly PMEs, GCEs, and even carbon paste electrodes with near to ideal slopes [11-25]. The most sensitive alkaline earth sensor has been reported to be a  $\text{Sr}^{2+}$  sensor having a potential slope of 30 mV dec<sup>-1</sup> of concentration, which was based on 1,13-diaza-2,3,11,12-dibenzo-4,7,10-trioxacyclopentadecane-14,15-dione [23] as the selective ion carrier, while the lowest detection limit belongs to a  $\text{Be}^{2+}$  selective 2,6-diphenyl-4-benzo-9-crown-3-pyridine sensor that was about  $4.0 \times 10^{-8}$  M [16].

Reports for the third and forth main groups are limited to  $\text{Al}^{3+}$  [26-29],  $\text{Tl}^+$  [30,31],  $\text{Sn}^{2+}$  sensors [32], while there have been a relatively large number of  $\text{Pb}^{2+}$  sensors [33-59]. Almost all of the mentioned sensors were PMEs; however, some reports on CGEs [48,50,51], and one report on a CWE (coated wire electrode) has also been developed [49].

The minimum detection limit is observed for a lead-selective CGE with a membrane composition of PVC:benzyl acetate: DMCDA18C6 (ionophore):oleic acid percent ratio of 30:49:6:15 [48]. Meanwhile, detection limits in the range of  $10^{-7}$  and  $10^{-6}$  M for lead sensors are very common.

It can be seen in Table 1 that transition and heavy metal ion sensors reported include a PMME (polymeric membrane microelectrodes) for  $\text{Y}^{3+}$  [60], three PMEs [61,63,64] and one CGE [62] for Vanadyl ion, eight PMEs for  $\text{Cr}^{3+}$  [65-72], one of which could also be used in the CGE mode [70], and two  $\text{Fe}^{3+}$  PMEs based on 5,10,15,20-tetrakis(pentafluorophenyl)-21H,23H-porphyrin [73] and 2-[(2-hydroxy-1-propenyl-but-1,3-dienylimino)-methyl]-4-p-tolylazo-phenol [74].

The other sensors include  $\text{Ni}^{2+}$  PMEs (and one CWE) based on dibenzodiaz-15-crown-4 [75], 2,5-thiophenyl bis(5-tert-butyl-1,3-benzoxazole) [76], 2-methyl-4-(4-methoxy-phenyl)-2,6-diphenyl-2H-thiopyran [77], 1,10-dibenzyl-1,10-diaza-18-crown-6 [78], 1,5-diphenyl-thiocarbazone [79], benzylbis(thiosemicarbazone) [80], 1,3,7,9,13,15,19,21-octaza-pentacyclooctacosane (pentacyclooctaaza) [81], N,N'-bis (4-dimethylamino-benzylidene)- benzene-1,2-

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**Table 1.** Cationic Sensors Published by the Iranian Researchers in the Past Decade

Cation	Ionophore	Slope (mV dec <sup>-1</sup> )	LR (M)	DL (M)	Cations with $\log K_{\text{Sel}} > -2$	Type	Ref.
Na <sup>+</sup>	Dibenzopyridino-18-crown-6	58.5	$10^{-4}$ - $10^{-1}$	$9.0 \times 10^{-5}$	K <sup>+</sup> , Cs <sup>+</sup> , NH <sub>4</sub> <sup>+</sup> , Pb <sup>2+</sup>	PME	[1]
K <sup>+</sup> -1	Styrene/4'-vinyl-benzo-24-crown-8 copolymer	57.0	$4.0 \times 10^{-6}$ - $1.0 \times 10^{-2}$	$1.0 \times 10^{-6}$	Li <sup>+</sup> , Na <sup>+</sup> , Cs <sup>+</sup>	PME	[2]
K <sup>+</sup> -2	1,10-Bis(2'-benzoic acid)-1,4,7,10-tetradecane and 1,7-Bis(2'-benzoic acid)-1,4,7-trioxaheptane	61.8 62.6	$3.1 \times 10^{-5}$ - $2.7 \times 10^{-2}$ $2.0 \times 10^{-5}$ - $7.3 \times 10^{-2}$	$1.0 \times 10^{-5}$ $4.0 \times 10^{-6}$	Na <sup>+</sup> , Ba <sup>2+</sup>	PME	[3]
K <sup>+</sup> -3	2,3,9,10-Dibenzo-6-hydroxy-1,4,8,11,14-pentaoxacyclohexadecane	57.0	$10^{-7}$ - $10^{-1}$	$1.0 \times 10^{-7}$	Ba <sup>2+</sup>	PME	[4]
Rb <sup>+</sup>	Dibenzo-21-crown-7	57.8 55.3	$5.0 \times 10^{-5}$ - $1.0 \times 10^{-1}$ $1.0 \times 10^{-5}$ - $5.0 \times 10^{-2}$	$1.5 \times 10^{-5}$ $7.1 \times 10^{-6}$	K <sup>+</sup> , Cs <sup>+</sup> , NH <sub>4</sub> <sup>+</sup>	PME CGE	[5]
Cs <sup>+</sup> -1	Derivative of gamma-pyrone	57.7	$10^{-5}$ - $10^{-3}$	$3.0 \times 10^{-5}$	Rb <sup>+</sup>	PME	[6]
Cs <sup>+</sup> -2	1,5-Diaza-2,3,4-naphthyl-8,11,14-trioxacyclohexadecane-6,16-dione	59.5	$6.9 \times 10^{-6}$ - $5.0 \times 10^{-1}$	$4.7 \times 10^{-6}$	Rb <sup>+</sup>	PME	[7]
Cs <sup>+</sup> -3	[25-(3-Bromo-propoxy)-5,11,-17,23-tetrakis(tert-butyl)-26,27,28-tris(1-propyloxy)calix-4[arene]]	57.5	$10^{-6}$ - $10^{-1}$	$2.1 \times 10^{-7}$	K <sup>+</sup> , Rb <sup>+</sup>	PME	[8]
Cs <sup>+</sup> -4	Poly (tetrafluoroethylene-co-ethylene-co-vinylacetate)	58.0	$10^{-4}$ - $10^{-1}$	$8.0 \times 10^{-5}$	Na <sup>+</sup> , NH <sub>4</sub> <sup>+</sup> , K <sup>+</sup>	ZM E	[9]
Cs <sup>+</sup> -5	7,11,15,28-Tetraiodo-1,21,23,25-tetramethyl-2,20:3,19-dimethano-1H,21H,23H,25H-bis[1,3]dioxocino[5,4-i:5',4'T]benzo[1,2-d:5,4-d']-bis[1,3]benzodioxocin stereoisomer	59.1	$10^{-5}$ - $10^{-1}$	$5.0 \times 10^{-6}$	Na <sup>+</sup> , Tl <sup>+</sup>	PME	[10]
Be <sup>2+</sup> -1	Benzo-9-crown-3	29.0	$2.5 \times 10^{-6}$ - $4 \times 10^{-3}$	$1.0 \times 10^{-6}$	Mg <sup>2+</sup> , Li <sup>+</sup> , K <sup>+</sup>	PME	[11]
Be <sup>2+</sup> -2	3,4-Di[2-(2-tetrahydro-2H-pyranoyl)]ethoxy styrene-styrene copolymer	29.0	$10^{-6}$ - $10^{-3}$	$8.0 \times 10^{-7}$	Ca <sup>2+</sup> , Mg <sup>2+</sup> , K <sup>+</sup>	PME	[12]
Be <sup>2+</sup> -3	2,4-Dinitrophenylhydrazine-benzo-9-crown-3	29.8	$10^{-6}$ - $10^{-1}$	$5.0 \times 10^{-7}$	-	PME	[13]
Be <sup>2+</sup> -4	Naphto-9-crown-3	29.5	$8.0 \times 10^{-6}$ - $10^{-1}$	$2.0 \times 10^{-7}$	-	PME	[14]
Be <sup>2+</sup> -5	2,4-Dinitrophenylhydrazine benzo-9-crown-3	29.5	$4.0 \times 10^{-7}$ - $10^{-1}$	$6.0 \times 10^{-6}$	-	PME	[15]
Be <sup>2+</sup> -6	2,6-Diphenyl-4-benzo-9-crown-3-pyridine	29.6	$10^{-7}$ - $10^{-1}$	$4.0 \times 10^{-8}$	Sr <sup>2+</sup> , Ba <sup>2+</sup> , Cd <sup>2+</sup>	CGE	[16]

**Table 1.** Continued

Be <sup>2+</sup> -7	2,3,5,6,8,9-Hexahydro-1,4,7,10-benzotetraoxacyclo dodecene -12-carbaldehyde-12-(2,4-dinitrophenyl)hy	29.9	10 <sup>-7</sup> -10 <sup>-1</sup>	7.0×10 <sup>-8</sup>	-	PME	[17]
Be <sup>2+</sup> -8	1,15-Diaza-3,4;12,13-dibenzo-5,8,11-trioxabicyclo[13.2.2]heptadecane-2,14-dione	29.4	3.0×10 <sup>-6</sup> -3.0×10 <sup>-2</sup>	2.0×10 <sup>-6</sup>	Ag <sup>+</sup> , Hg <sup>2+</sup>	PME	[18]
		29.4	5.0×10 <sup>-7</sup> -2.0×10 <sup>-2</sup>	4.0×10 <sup>-7</sup>	CGE		
Be <sup>2+</sup> -9	A benzo-9-crown-3 derivative	29.5	10 <sup>-7</sup> -10 <sup>-1</sup>	8.0×10 <sup>-8</sup>	-	CGE	[19]
Ca <sup>2+</sup> -1	1,4-Diaza-2,3;8,9-dibenzo-7,10-dioxacyclododecane-5,12-dione	32.0	1.3×10 <sup>-6</sup> -3.2×10 <sup>-3</sup>	7.9×10 <sup>-7</sup>	Cd <sup>2+</sup> , Co <sup>2+</sup>	CPE	[20]
Ca <sup>2+</sup> -2	2-[(2-Hydroxyphenyl)imino]-1,2-diphenylethanone	28.5	10 <sup>-6</sup> -10 <sup>-1</sup>	8.0×10 <sup>-7</sup>	Li <sup>+</sup>	PME	[21]
Ca <sup>2+</sup> -3	Dimethyl-1-(4-nitrobenzoyl)-8-oxo-2,8-dihydro-1H-pyrazolo[5,1-a]isoindole-2,3-dicarboxylate	29.5	8.0×10 <sup>-7</sup> -10 <sup>-3</sup>	5.0×10 <sup>-7</sup>	-	PME	[22]
Sr <sup>2+</sup> -1	1,13-Ddiaza-2,3,11,12-dibenzo-4,7,10-trioxacyclopentadecane-14,15-dione	30.0	3.2×10 <sup>-5</sup> -10 <sup>-1</sup>	8.0×10 <sup>-6</sup>	K <sup>+</sup> , Ca <sup>2+</sup> , Pb <sup>2+</sup>	PME	[23]
Sr <sup>2+</sup> -2	Dibenzo-30-crown-10	29.2	10 <sup>-5</sup> -10 <sup>-3</sup>	5.0×10 <sup>-6</sup>	K <sup>+</sup>	PME	[24]
Ba <sup>2+</sup>	Dimethyl-1-acetyl-8-oxo-2,8-dihydro-1H-pyrazolo[5,1-a]isoindole-2,3-dicarboxylate	29.7	10 <sup>-6</sup> -10 <sup>-1</sup>	7.6×10 <sup>-7</sup>	-	PME	[25]
Al <sup>3+</sup> -1	Ethandione, di-(2-furyl) (Furil)	18.5	10 <sup>-6</sup> -10 <sup>-2</sup>	1.3×10 <sup>-7</sup>	Cu <sup>2+</sup> , Cd <sup>2+</sup> , Hg <sup>2+</sup> , Ba <sup>2+</sup>	PME	[26]
Al <sup>3+</sup> -2	Bis(5-phenylazosalicylaldehyde)-2,3-naphthalene diamine	19.8	5.0×10 <sup>-6</sup> -10 <sup>-2</sup>	2.5×10 <sup>-6</sup>	Fe <sup>3+</sup> , Mg <sup>2+</sup> , NH <sub>4</sub> <sup>+</sup> , Ag <sup>+</sup>	PME	[27]
Al <sup>3+</sup> -3	1-Hydroxy-3-methyl-thiocanthone	19.7	2.0×10 <sup>-6</sup> -2.0×10 <sup>-2</sup>	1.0×10 <sup>-6</sup>	Fe <sup>3+</sup> , Hg <sup>2+</sup> , Cu <sup>2+</sup>	PME	[28]
Al <sup>3+</sup> -4	1-Hydroxy-3-methyl-9H-xanthen-9-one	20.0	10 <sup>-6</sup> -1.6×10 <sup>-1</sup>	6.0×10 <sup>-7</sup>	NH <sub>4</sub> <sup>+</sup> , Ag <sup>+</sup> , K <sup>+</sup> , Na <sup>+</sup>	PME	[29]
Tl <sup>+</sup> -1	1,21,23,25-Tetramethyl-2,20:3,19-dimetheno-[H <sub>2</sub> ] H <sub>23</sub> H, 25H-bis-[1,3] dioxocino[5,4-i:5',4'-i] benzo [1,2d:5,4-d'] bis[1,3] benzodioxocin(II)	59.8	10 <sup>-5</sup> -10 <sup>-1</sup>	5.0×10 <sup>-6</sup>	Ag <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup>	PME	[30]
Tl <sup>+</sup> -2	Dibenzylidaza-18-crown-6	56.9	10 <sup>-5</sup> -10 <sup>-1</sup>	5.0×10 <sup>-6</sup>	K <sup>+</sup> , Ag <sup>+</sup> , NH <sup>4+</sup> , Zn <sup>2+</sup> , Co <sup>2+</sup>	PME	[31]
Sn <sup>2+</sup>	Dibenzo-18-crown-6	27.5	10 <sup>-6</sup> -10 <sup>-2</sup>	8.0×10 <sup>-7</sup>	Fe <sup>2+</sup> , Mg <sup>2+</sup> , Hg <sup>2+</sup> , Ca <sup>2+</sup> , Bi <sup>2+</sup>	PME	[32]

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**Table 1.** Continued

Pb <sup>2+</sup> -1	Dibenzopyridino-18-crown-6	N	10 <sup>-5</sup> -10 <sup>-1</sup>	4.0×10 <sup>-5</sup>	-	PME	[33]
Pb <sup>2+</sup> -2	1,8-Dihydroxy-2,7-bis(prop-2'-enyl)-9,10-antraquinone	29.1	2.0×10 <sup>-6</sup> -2.0×10 <sup>-3</sup>	1.1×10 <sup>-6</sup>	Cu <sup>2+</sup>	PME	[34]
Pb <sup>2+</sup> -3	5,5'-Dithiobis-(2-nitrobenzoic acid)	29.0	4.0×10 <sup>-6</sup> -10 <sup>-2</sup>	1.5×10 <sup>-6</sup>	Ag <sup>+</sup> , Tl <sup>+</sup> , Cd <sup>2+</sup> , Hg <sup>2+</sup>	PME	[35]
Pb <sup>2+</sup> -4	4'-Vinylbenzo-15-crown-5 homopolymer	29.0	10 <sup>-6</sup> -4.0×10 <sup>-3</sup>	7.0×10 <sup>-7</sup>	Na <sup>+</sup> , K <sup>+</sup> , Rb <sup>+</sup> , Cs <sup>+</sup> , Ag <sup>+</sup>	PME	[36]
Pb <sup>2+</sup> -5	Bis[(1-hydroxy-9,10-antraquinone)-2-methyl]sulfide	29.0	4.0×10 <sup>-6</sup> -5.6×10 <sup>-3</sup>	7.0×10 <sup>-7</sup>	Cu <sup>2+</sup> , Hg <sup>2+</sup>	PME	[37]
Pb <sup>2+</sup> -6	Benzyl disulphide	29.2	2.0×10 <sup>-5</sup> -5.0×10 <sup>-2</sup>	1.0×10 <sup>-5</sup>	Na <sup>+</sup> , Ag <sup>+</sup> , Zn <sup>2+</sup> , Cd <sup>2+</sup>	PME	[38]
Pb <sup>2+</sup> -7	Cryptand (222)	23.0	10 <sup>-5</sup> -10 <sup>-1</sup>	5.0×10 <sup>-6</sup>	K <sup>+</sup> , Na <sup>+</sup> , Al <sup>3+</sup> , Zn <sup>2+</sup>	PME	[39]
Pb <sup>2+</sup> -8	1,4-Bis (prop-2'-enyloxy)-9,10-antraquinone	29.8	2.5×10 <sup>-6</sup> -10 <sup>-2</sup>	1.5×10 <sup>-6</sup>	Ag <sup>+</sup> , Fe <sup>3+</sup>	PME	[40]
Pb <sup>2+</sup> -9	1,10-Dibenzyl-1,10-diaza-18-crown-6	29.3	5.0×10 <sup>-5</sup> -10 <sup>-2</sup>	2.8×10 <sup>-5</sup>	Tl <sup>+</sup> , NH <sub>4</sub> <sup>+</sup> , K <sup>+</sup> , Li <sup>+</sup>	PME	[41]
Pb <sup>2+</sup> -10	Dimethyl-benzo-tetrathia-fulvalene	28.5	10 <sup>-5</sup> -10 <sup>-2</sup>	8.0×10 <sup>-6</sup>	Ni <sup>2+</sup> , Cu <sup>2+</sup>	PME	[42]
Pb <sup>2+</sup> -11	Tetraphenylporphyrin	30.0	10 <sup>-5</sup> -10 <sup>-2</sup>	8.5×10 <sup>-6</sup>	Cu <sup>2+</sup> , Ca <sup>2+</sup> , Sr <sup>2+</sup>	PME	[43]
Pb <sup>2+</sup> -12	Capric acid	29.0	10 <sup>-5</sup> -10 <sup>-2</sup>	6.0×10 <sup>-6</sup>	Ag <sup>+</sup> , K <sup>+</sup> , Na <sup>+</sup> , Li <sup>+</sup>	PME	[44]
Pb <sup>2+</sup> -13	Hexathia-18-crown-6-tetraone	29.0	10 <sup>-6</sup> -8.0×10 <sup>-3</sup>	8.0×10 <sup>-7</sup>	Hg <sup>2+</sup>	PME	[45]
Pb <sup>2+</sup> -14	Piroxicam	30.0	10 <sup>-5</sup> -10 <sup>-1</sup>	4.0×10 <sup>-6</sup>	Ag <sup>+</sup> , Na <sup>+</sup> , Al <sup>3+</sup> , Cu <sup>2+</sup>	PME	[46]
Pb <sup>2+</sup> -15	Phenyl disulfide	29.3	2.0×10 <sup>-6</sup> -10 <sup>-2</sup>	1.2×10 <sup>-6</sup>	Cu <sup>2+</sup> , Ag <sup>+</sup>	PME	[47]
Pb <sup>2+</sup> -16	N,N'-Dimethylcyanodiazia-18-crown-6	29.0	10 <sup>-7</sup> -10 <sup>-2</sup>	7.0×10 <sup>-8</sup>	-	CGE	[48]
Pb <sup>2+</sup> -17	N,N-Bis(5-methyl salicylidine)- <i>p</i> -diphenylene methane diamine	29.4	2.0×10 <sup>-5</sup> -10 <sup>-1</sup>	2.0×10 <sup>-6</sup>	Zn <sup>2+</sup> , Fe <sup>3+</sup> , K <sup>+</sup> , NH <sub>4</sub> <sup>+</sup>	CWE	[49]
Pb <sup>2+</sup> -18	2-(2-Ethanoloxymethyl)-1-hydroxy-9,10-antraquinone	29.5	10 <sup>-7</sup> -10 <sup>-2</sup>	8.0×10 <sup>-8</sup>	Hg <sup>2+</sup> , Ag <sup>+</sup>	CGE	[50]
Pb <sup>2+</sup> -19	1-Hydroxy-{2-2-[2-(2-hydroxyethoxy)-ethoxy]-ethoxymethyl}-anthracene-9,10-dione	32.5	10 <sup>-6</sup> -10 <sup>-1</sup>	5.0×10 <sup>-7</sup>	Hg <sup>2+</sup> , Ag <sup>+</sup> , Tl <sup>+</sup>	CGE	[51]
Pb <sup>2+</sup> -20	2,2'-Dithiodibenzoic acid	29.9	5.0×10 <sup>-6</sup> -4.0×10 <sup>-2</sup>	2.0×10 <sup>-6</sup>	Hg <sup>2+</sup> , Cu <sup>2+</sup>	PME	[52]
Pb <sup>2+</sup> -21	N,N'-Bis(3-methylsalicylidine)- <i>p</i> -phenyl methane diamine	30.3	2.0×10 <sup>-5</sup> -10 <sup>-1</sup>	1.0×10 <sup>-5</sup>	Na <sup>+</sup> , K <sup>+</sup> , NH <sub>4</sub> <sup>+</sup>	CWE	[53]
Pb <sup>2+</sup> -22	Dibenzodiaza-15-crown-4	29.5	5.0×10 <sup>-6</sup> -10 <sup>-2</sup>	3.5×10 <sup>-6</sup>	Cu <sup>2+</sup> , Co <sup>2+</sup>	PME	[54]

**Table 1.** Continued

Pb <sup>2+</sup> -23	Oxim phenyl 2-keto methyl quinoline	26.8	$10^{-5}$ - $10^{-1}$	$1.0 \times 10^{-5}$	Cu <sup>2+</sup> , Ag <sup>+</sup>	PME	[55]
Pb <sup>2+</sup> -24	1,10-Dibenzyl-1,10-diaza-18-crown-6	29.1	$5.0 \times 10^{-6}$ - $10^{-1}$	$3.0 \times 10^{-6}$	Cd <sup>2+</sup> , Cu <sup>2+</sup>	Sol-gel	[56]
		28.9		$5.0 \times 10^{-6}$		CWE	
Pb <sup>2+</sup> -25	9,10-Anthraquinone derivatives	28.9	$10^{-6}$ - $10^{-2}$	$6.7 \times 10^{-7}$	Zn <sup>2+</sup> , Cd <sup>2+</sup>	PME	[57]
Pb <sup>2+</sup> -26	1-Phenyl-2-(2-quinolyl)-1,2-dioxo-2-(4-bromo) phenylhydrazone	28.7	$10^{-6}$ - $10^{-1}$	$6.0 \times 10^{-7}$	Hg <sup>2+</sup> , Ag <sup>+</sup> , Cu <sup>2+</sup>	PME	[58]
Pb <sup>2+</sup> -27	Bis(2-hydroxyacetophenone) ethylenediamine	29.4	$10^{-5}$ - $10^{-1}$	$5.0 \times 10^{-5}$	Na <sup>+</sup> , K <sup>+</sup> , Cu <sup>2+</sup>	CWE	[59]
Y <sup>3+</sup>	(2-( <i>{(E)}</i> 1,2-Diphenyl-2-[ <i>{(2-2-sulfanylphenyl)imino}ethylidene</i> ]amino)-1-benzenethiol	19.2	$10^{-7}$ - $10^{-2}$	$7.0 \times 10^{-8}$	Sc <sup>3+</sup>	PMME	[60]
VO <sup>2+</sup> -1	1,8-Diaminonaphthalene	29.7	$10^{-5}$ - $10^{-1}$	$7.9 \times 10^{-6}$	Fe <sup>3+</sup> , Ag <sup>+</sup>	PME	[61]
VO <sup>2+</sup> -2	1,8-Diaminonaphthalene	28.3	$1.4 \times 10^{-7}$ - $1.4 \times 10^{-1}$	$1.4 \times 10^{-7}$	Fe <sup>3+</sup> , Al <sup>3+</sup> , UO <sub>2</sub> <sup>2+</sup>	CGE	[62]
VO <sup>2+</sup> -3	A calix[4]arene derivative	29.9	$10^{-5}$ - $10^{-1}$	$3.9 \times 10^{-6}$	Tl <sup>+</sup> , Na <sup>+</sup> , Li <sup>+</sup> , NH <sub>4</sub> <sup>+</sup> , Cs <sup>+</sup>	PME	[63]
VO <sup>2+</sup> -4	Vanadyl phosphate	29.5	$10^{-6}$ - $10^{-1}$	$1.0 \times 10^{-7}$	Ca <sup>2+</sup> , K <sup>+</sup>	PME	[64]
VO <sup>2+</sup> -5	4-Dimethylaminoazobenzene	19.5	$1.66 \times 10^{-6}$ - $10^{-2}$	$8.0 \times 10^{-7}$	Ag <sup>+</sup> , Mn <sup>2+</sup> , K <sup>+</sup> , Fe <sup>3+</sup> , V <sup>4+</sup>	PME	[65]
Cr <sup>3+</sup> -1	4-Hydroxysalicylade-2-mercaptoanil	20.2	$3.0 \times 10^{-6}$ - $10^{-1}$	$1.5 \times 10^{-6}$	-	PME	[66]
Cr <sup>3+</sup> -2	Glyoxal bis(2-hydroxyanil)	19.8	$3.0 \times 10^{-6}$ - $10^{-2}$	$6.3 \times 10^{-7}$	Cu <sup>2+</sup> , Cr <sup>6+</sup> , Zn <sup>2+</sup> , Co <sup>2+</sup>	PME	[67]
Cr <sup>3+</sup> -3	2,3,8,9-Tetraphenyl-1,4,7,10-tetra-azacyclododeca-1,3,7,9-tetraene	19.5	$10^{-6}$ - $10^{-1}$	$7.0 \times 10^{-7}$	Ag <sup>+</sup>	PME	[68]
Cr <sup>3+</sup> -4	Oxalic acid bis(cyclohexylidene hydrazide)	19.8	$10^{-7}$ - $10^{-2}$	$3.0 \times 10^{-8}$	Ni <sup>2+</sup> , Cd <sup>2+</sup>	PME	[69]
Cr <sup>3+</sup> -5	2-Hydroxybenzaldehyde-O,O'- (1,2-dioxetane-1,2-diyl) oxime	19.6	$1.5 \times 10^{-6}$ - $8.0 \times 10^{-3}$	$1.5 \times 10^{-6}$	-	PME	[70]
Cr <sup>3+</sup> -6	N-(1-Thien-2-ylethylidene) benzene-1,2-diamine	19.2	$4.0 \times 10^{-7}$ - $3.0 \times 10^{-3}$	$2.0 \times 10^{-7}$		CGCE	
		19.9	$10^{-6}$ - $10^{-1}$	$7.0 \times 10^{-7}$	Fe <sup>3+</sup>	PME	[71]
Cr <sup>3+</sup> -7	4-Amino-3-hydrazino-6-methyl-1,2,4-triazin-5-one	19.7	$10^{-6}$ - $10^{-1}$	$5.8 \times 10^{-7}$	La <sup>3+</sup> , Ce <sup>3+</sup> , Al <sup>3+</sup>	PME	[72]
Fe <sup>3+</sup> -1	5,10,15,20-Tetrakis (penta-fluorophenyl)-21H,23H-porphyrin	25.0	$10^{-6}$ - $10^{-4}$	$6.3 \times 10^{-7}$	Ag <sup>+</sup> , Na <sup>+</sup> , Li <sup>+</sup>	PME	[73]
Fe <sup>3+</sup> -2	2-[ <i>{(2-Hydroxy-1-propenyl-but-1,3-dienylimino)methyl}</i> ]-4- <i>p</i> -tolylazo-phenol	28.5	$3.5 \times 10^{-6}$ - $4.0 \times 10^{-2}$	$6.3 \times 10^{-7}$	Cu <sup>2+</sup> , Zn <sup>2+</sup>	PME	[74]

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**Table 1.** Continued

Ni <sup>2+</sup> -1	Dibenzodiaza-15-crown-4	30.3	7.1×10 <sup>-7</sup> -1.2×10 <sup>-2</sup>	5.6×10 <sup>-7</sup>	Ag <sup>+</sup> , Cu <sup>2+</sup> , Co <sup>2+</sup> , Zn <sup>2+</sup> , Pb <sup>2+</sup> , Cd <sup>2+</sup>	PME	[75]
Ni <sup>2+</sup> -2	2,5-Thiophenyl bis(5-tert-butyl-1,3-benzoxazole)	29.5	10 <sup>-5</sup> -10 <sup>-2</sup>	8.0×10 <sup>-6</sup>	Co <sup>2+</sup> , Na <sup>+</sup> , Pb <sup>2+</sup>	PME	[76]
Ni <sup>2+</sup> -3	2-Methyl-4-(4-methoxy phenyl)-2,6-diphenyl-2H-thiopyran	29.5	2.0×10 <sup>-5</sup> -5.0×10 <sup>-2</sup>	9.0×10 <sup>-6</sup>	Zn <sup>2+</sup> , Co <sup>2+</sup>	PME	[77]
Ni <sup>2+</sup> -4	1,10-Dibenzyl-1,10-diaza-18-crown-6	29.8	2.0×10 <sup>-5</sup> -5.5×10 <sup>-2</sup>	1.2×10 <sup>-5</sup>	Li <sup>+</sup> , K <sup>+</sup> , Cd <sup>2+</sup>	PME	[78]
Ni <sup>2+</sup> -5	1,5-Diphenylthiocarbazone	29.5	5.0×10 <sup>-6</sup> -10 <sup>-2</sup>	2.8×10 <sup>-6</sup>	Ba <sup>2+</sup> , Mg <sup>2+</sup>	PME	[79]
Ni <sup>2+</sup> -6	Benzylbis(thiosemicarbazone)	29.0	10 <sup>-7</sup> -10 <sup>-2</sup>	4.0×10 <sup>-8</sup>	-	CGE	[80]
Ni <sup>2+</sup> -7	1,3,7,9,13,15,19,21-Octaazapentacyclooctacosane (pentacyclooctaaza)	30.5	10 <sup>-6</sup> -10 <sup>-1</sup>	6.0×10 <sup>-7</sup>	Ba <sup>2+</sup>	CWE	[81]
Ni <sup>2+</sup> -8	N,N'-Bis-(4-dimethylamino-benzylidene)-benzene-1,2-diamine	30.0	10 <sup>-7</sup> -10 <sup>-2</sup>	8.0×10 <sup>-8</sup>	Hg <sup>2+</sup> , Ag <sup>+</sup>	PME	[82]
Ni <sup>2+</sup> -9	Mercapto compound	28-30	10 <sup>-7</sup> -10 <sup>-2</sup>	6.0×10 <sup>-8</sup>	Cu <sup>2+</sup> , Co <sup>2+</sup>	PME	[83]
Pd <sup>2+</sup>	Hexadecylpyridinium ion	29.4	2.5×10 <sup>-3</sup> -5.2×10 <sup>-6</sup>	1.0×10 <sup>-6</sup>	Pt <sup>2+</sup>	PME	[84]
Co <sup>2+</sup> -1	9-t-Butyl-3,9,15,21-tetraaza-4,5;13,14-dibenzo-6,12-dioxabicyclo[15.3.1]henicosa-1(21),17,19-triene-2,16-dione	29.45	2.0×10 <sup>-6</sup> -10 <sup>-2</sup>	6.0×10 <sup>-7</sup>	Ni <sup>2+</sup> , Cu <sup>2+</sup>	PME	[85]
		29.45					
Co <sup>2+</sup> -2	(2-Mercapto-4-methylphenyl)-2-benzamido-3-phenylthiopropenoate	30.0	4.0×10 <sup>-7</sup> -10 <sup>-2</sup>	1.0×10 <sup>-7</sup>	Cu <sup>2+</sup> , Cd <sup>2+</sup> , Ag <sup>+</sup> , Tl <sup>+</sup>	PME	[86]
Co <sup>2+</sup> -3	9-t-Butyl-3,9,15,21-tetraaza-4,5;13,14-dibenzo-6,12-dioxabicyclo[15.3.1]henicosa-1(21),17,19-triene-2,16-dione	29.1	7.0×10 <sup>-7</sup> -10 <sup>-2</sup>	2.0×10 <sup>-7</sup>	Ag <sup>+</sup> , Ni <sup>2+</sup>	CGE	[87]
Co <sup>2+</sup> -4	5-((4-Nitrophenyl)azo)-N-(2',4'-dimethoxyphenyl)salicylaldimine	29.0	9.0×10 <sup>-7</sup> -10 <sup>-2</sup>	8.0×10 <sup>-7</sup>	Cu <sup>2+</sup> , Hg <sup>2+</sup> , Cd <sup>2+</sup>	PME	[88]
Co <sup>2+</sup> -5	Oxime of 1-(2-oxocyclohexyl)-1,2-cyclohexanediol	29.8	10 <sup>-6</sup> - 10 <sup>-1</sup>	9.0×10 <sup>-7</sup>	-	PME	[89]
Cu <sup>2+</sup> -1	Naphthol-derivative Schiff's base	29.8	5.0×10 <sup>-6</sup> -5.0×10 <sup>-2</sup>	3.1×10 <sup>-6</sup>	Na <sup>+</sup> , Ni <sup>2+</sup> , Hg <sup>2+</sup>	PME	[90]
Cu <sup>2+</sup> -2	1,15-Diaza-3,4;12,13-dibenzo-5,8,11,18,21-pentaoxacyclotriecosane-2,14-dione	30.0	3.2×10 <sup>-5</sup> -10 <sup>-2</sup>	1.2×10 <sup>-6</sup>	Na <sup>+</sup> , K <sup>+</sup> , Sr <sup>2+</sup> , Cs <sup>+</sup>	PME	[91]
Cu <sup>2+</sup> -3	Thiophene-derivative Schiff base	29.3	6.0×10 <sup>-8</sup> -10 <sup>-1</sup>	2.0×10 <sup>-8</sup>	Zn <sup>2+</sup> , Hg <sup>2+</sup>	PME	[92]

**Table 1.** Continued

Cu <sup>2+</sup> -4	Mixed aza-thioether crowns containing a 1,10-phenanthroline sub-unit	29.4	10 <sup>-5</sup> - 2.0×10 <sup>-1</sup>	8.0×10 <sup>-6</sup>	La <sup>3+</sup> , Ag <sup>+</sup>	PME	[93]
Cu <sup>2+</sup> -5	Bis-2-thiophenal propanediamine	29.1	6.0×10 <sup>-8</sup> -10 <sup>-1</sup>	3.0×10 <sup>-8</sup>	-	CGE	[94]
Cu <sup>2+</sup> -6	2,2'-Dithiodianiline	30.0	7.0 ×10 <sup>-7</sup> -5.0×10 <sup>-2</sup>	6.0×10 <sup>-6</sup>	Pd <sup>2+</sup>	PME	[95]
Cu <sup>2+</sup> -7	Diphenylisocyanate bis(acetylacetone)ethylenedinnine	29.8	10 <sup>-6</sup> -10 <sup>-1</sup>	6.0×10 <sup>-7</sup>	-	PME	[96]
Cu <sup>2+</sup> -8	3,6,9,14-Tetrathiabicyclo [9.2.1]tetradeca-11,13-diene	28.0	6.3×10 <sup>-7</sup> -2.5×10 <sup>-1</sup>	3.2×10 <sup>-7</sup>	Ag <sup>+</sup>	PME	[97]
Cu <sup>2+</sup> -9	1-Hydroxy-2-(prop-2'-enyl)-4-(prop-2'-enoxy)-9,10-anthraquinone	27.3 29.1	10 <sup>-5</sup> -10 <sup>-1</sup> 8.0×10 <sup>-8</sup> -5.0×10 <sup>-2</sup>	8.0×10 <sup>-6</sup> 5.0 ×10 <sup>-8</sup>	Zn <sup>2+</sup> , Pb <sup>2+</sup>	PME CGE	[98]
Cu <sup>2+</sup> -10	2-Quinolyl-2-phenylglyoxal-2-oxime(phenylglyoxal-alpha-monoxime)	28.2	10 <sup>-6</sup> -10 <sup>-1</sup>	5.0×10 <sup>-7</sup>	Fe <sup>3+</sup> , Al <sup>3+</sup> , K <sup>+</sup>	CWE	[99]
Cu <sup>2+</sup> -11	1,3-Dithiane,2-(4-methoxyphenyl)	29.5	3.0×10 <sup>-6</sup> -5.0×10 <sup>-2</sup>	1.0×10 <sup>-6</sup>	K <sup>+</sup> , Hg <sup>2+</sup> , Ag <sup>+</sup>	PME	[100]
Cu <sup>2+</sup> -12	2,2'-[4,4'-Diphenyl-methane bis(nitrilomethylidyne)]-bisphenol	29.5	8.0×10 <sup>-6</sup> -10 <sup>-1</sup>	3.0×10 <sup>-6</sup>	Pb <sup>2+</sup>	PME	[101]
Cu <sup>2+</sup> -13	1,3-Dithiane,2-(4-methoxy phenyl)	29.5	3.0 ×10 <sup>-6</sup> -5.0×10 <sup>-2</sup>	1.0×10 <sup>-6</sup>	Ag <sup>+</sup> , Pb <sup>2+</sup> , Na <sup>+</sup>	PME	[102]
Cu <sup>2+</sup> -14	2-(1'-(4'-(1"-Hydroxy-2"-naphthyl)methyleneamino)butyl iminomethyl)-1-naphthol	29.0	10 <sup>-6</sup> -10 <sup>-1</sup>	8.0×10 <sup>-7</sup>	Tl <sup>+</sup>	PME	[103]
Cu <sup>2+</sup> -15	N,N'-Ethylene bis(p-tert-butyl salicylaldiminato)	29.5	4.0×10 <sup>-6</sup> -10 <sup>-1</sup>	1.5×10 <sup>-6</sup>	Pb <sup>2+</sup>	CWE	[104]
Cu <sup>2+</sup> -16	Thiosemicarbazone	29.2 28.1	6.0×10 <sup>-6</sup> -10 <sup>-1</sup> 10 <sup>-5</sup> -10 <sup>-1</sup>	6.0×10 <sup>-6</sup> 3.0×10 <sup>-6</sup>	Hg <sup>2+</sup> , Pb <sup>2+</sup>	Sol-gel CWE	[105]
Cu <sup>2+</sup> -17	6-Methyl-4-(1-phenylmethylidene) amino-3-thioxo-1,2,4-triazin-5-one	29.2	10 <sup>-6</sup> -10 <sup>-1</sup>	4.8×10 <sup>-7</sup>	Ca <sup>2+</sup> , Sr <sup>2+</sup>	PME	[106]
Cu <sup>2+</sup> -18	4-Amino-6-methyl-1,2,4-triazin-5-one-3-thione	29.3	10 <sup>-6</sup> -10 <sup>-1</sup>	6.2×10 <sup>-7</sup>	Hg <sup>2+</sup> , Fe <sup>3+</sup> , Na <sup>+</sup>	PME	[107]
Cu <sup>2+</sup> -19	2-Mercaptobenzoxazole	29.2	5.0 ×10 <sup>-6</sup> -1.6×10 <sup>-2</sup>	2.0×10 <sup>-6</sup>	Ni <sup>2+</sup> , Pb <sup>2+</sup>	PME	[108]
Cu <sup>2+</sup> -20	2,2-[1,2-Ethandiyl-bis(nitrilo-methylidine)-bis]meta cresole(I), 2,2-[1,2-ethandiyl-bis(nitrilo-methylidine)-bis]para cresole(II) and 2,2'-[1,2-ethandiyl-bis(nitrite-methylidine)-bis]ortho cresole(III)	29.2 29.7 28.2	10 <sup>-5</sup> -10 <sup>-1</sup>	3.6×10 <sup>-6</sup> 3.1 ×10 <sup>-6</sup> 6.3 ×10 <sup>-6</sup>	Ni <sup>2+</sup> , Co <sup>2+</sup>	PME	[109]

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**Table 1.** Continued

Cu <sup>2+</sup> -21	2-{1-(E)-2-((Z)-2-{(E)-2-[(Z)-1-(2-Hydroxyphenyl)ethylidene]hydrazono}-1-methylpropylidene)hydrazono}ethyl}phenol	25.9	10 <sup>-11</sup> -10 <sup>-5</sup>	5.0×10 <sup>-12</sup>	-	PMME	[110]
Cu <sup>2+</sup> -22	1,8-Bis(2-hydroxynaphthal-diminato)-3,6-dioxaoctane	29.0	3.3×10 <sup>-6</sup> - 1.0	1.0×10 <sup>-6</sup>	Ag <sup>+</sup> , Na <sup>+</sup> , Al <sup>3+</sup>	CWE	[111]
Cu <sup>2+</sup> -23	2,2'-[1,9-Nonanediyl bis(nitrilo-ethylidyne)]-bis-(I-naphthol)	29.0	10 <sup>-6</sup> -5.0 ×10 <sup>-3</sup>	8.0×10 <sup>-7</sup>	Pb <sup>2+</sup> , Zn <sup>2+</sup> , Fe <sup>3+</sup>	PME	[112]
Ag <sup>+</sup> -1	hexathia-18-crown-6	59.0	6.0×10 <sup>-6</sup> -3.2×10 <sup>-3</sup>	4.0×10 <sup>-6</sup>	Tl <sup>+</sup> , K <sup>+</sup> , Na <sup>+</sup> , NH <sub>4</sub> <sup>+</sup> , Pb <sup>2+</sup>	PME	[113]
Ag <sup>+</sup> -2	Mixed aza-thioether crowns containing a 1,10-phenanthroline sub-unit	59.1	10 <sup>-5</sup> -10 <sup>-1</sup> 5.0×10 <sup>-8</sup> -4.0×10 <sup>-2</sup>	8.0×10 <sup>-6</sup> 3.0 ×10 <sup>-9</sup>	Tl <sup>+</sup> , Cu <sup>2+</sup>	CONISE SCISE	[114]
Ag <sup>+</sup> -3	Mixed aza-thioether crowns containing a 1,10-phenanthroline sub-unit	59.1	1.0×10 <sup>-6</sup> -1.0×10 <sup>-1</sup>	1.0×10 <sup>-8</sup>	Tl <sup>+</sup> , Pb <sup>2+</sup>	PME	[115]
		58.8	3.0×10 <sup>-8</sup> -5.0×10 <sup>-2</sup>	8.0×10 <sup>-7</sup>		CGE	
Ag <sup>+</sup> -4	2-Mercaptobenzimidazole and 2-mercaptopbenzothiazole	60.2 57.8	10 <sup>-6</sup> -10 <sup>-2</sup> 4.0 ×10 <sup>-7</sup>	6.3×10 <sup>-7</sup> 4.0 ×10 <sup>-7</sup>	Hg <sup>2+</sup> , K <sup>+</sup>	CGE	[116]
Ag <sup>+</sup> -5	2,c-8,c-14,c-20-Tetrabutyl-4,6,10,12,16,18,22,24-octaacetyl-resorc[4]arene	58.0	10 <sup>-5</sup> -10 <sup>-1</sup>	3.0×10 <sup>-6</sup>	-	CWE	[117]
Ag <sup>+</sup> -6	Thia-substituted macrocyclic diamide	60.2	1.7×10 <sup>-6</sup> -10 <sup>-1</sup>	7.0×10 <sup>-7</sup>	Hg <sup>2+</sup>	PME	[118]
Ag <sup>+</sup> -7	C-Methylcalix[4]resorcareneoctamethyl ester	60.0	10 <sup>-5</sup> -10 <sup>-1</sup> , 10 <sup>-7</sup> -10 <sup>-1</sup>	4.7×10 <sup>-6</sup> 8.5×10 <sup>-8</sup>	Tl <sup>+</sup> , Cs <sup>+</sup>	PME CGE	[119]
Ag <sup>+</sup> -8	Methyl-2-pyridyl ketone oxime, phenyl-2-pyridyl ketone oxime and bis[2-(o-carboxythiophenoxy)methyl]-4-bromo-1-methoxy-benzene	59.8- 60	10 <sup>-6</sup> -10 <sup>-1</sup>	5.0×10 <sup>-7</sup>	-	CGE	[120]
Ag <sup>+</sup> -9	Octahydroxycalix[4]arene derivative	58.0	3.3×10 <sup>-6</sup> -3.3×10 <sup>-2</sup>	2.1×10 <sup>-6</sup>	K <sup>+</sup>	PME	[121]
Ag <sup>+</sup> -10	Meso-tetraphenylporphine [H <sub>2</sub> T(4-OCH <sub>3</sub> )PP]	59.4	10 <sup>-6</sup> -10 <sup>-1</sup>	1.0×10 <sup>-6</sup>	Pb <sup>2+</sup>	PME	[122]
Ag <sup>+</sup> -11	2-[(2-{2-[(2-Carboxyphenyl)sulfanyl]ethoxy}ethyl)sulfanyl]benzoic acid	59.0	2.0×10 <sup>-8</sup> -10 <sup>-2</sup>	1.2×10 <sup>-8</sup>	Hg <sup>2+</sup>	CWE	[123]
Ag <sup>+</sup> -12	N,N'-Bis(2-thienylmethylene)-1,2-diaminobenzene	59.7	10 <sup>-6</sup> -10 <sup>-1</sup>	6.0×10 <sup>-7</sup>	Hg <sup>2+</sup> , Fe <sup>3+</sup>	CWE	[124]

**Table 1.** Continued

Ag <sup>+</sup> -13	Cone shaped calix[4]arene	58.2	$8.0 \times 10^{-6}$ - $10^{-1}$	$5.0 \times 10^{-6}$	-	PME	[125]
Ag <sup>+</sup> -14	2-Methyl-2,4-di(2-thienyl)-2,3-dihydro-1H-1,5-benzodiazepine	58.5	$10^{-6}$ - $10^{-1}$	$5.0 \times 10^{-7}$	-	PME	[126]
Ag <sup>+</sup> -15	[Bis 5-(4-nitrophenyl azo) salisylaldimine]-1,8-diamino, 3, 6-dioxooctane	56.2	$1.9 \times 10^{-6}$ - $2.7 \times 10^{-2}$	$7.8 \times 10^{-7}$	K <sup>+</sup> , NH <sub>4</sub> <sup>+</sup>	CPE	[127]
		58.4	$9.0 \times 10^{-7}$ - $3.1 \times 10^{-2}$	$4.2 \times 10^{-7}$		CWE	
Zn <sup>2+</sup> -1	Cryptand C2 <sub>B</sub> 22	24.0	$5.0 \times 10^{-5}$ - $5.0 \times 10^{-2}$	$3.98 \times 10^{-5}$	Na <sup>+</sup> , K <sup>+</sup> , NH <sub>4</sub> <sup>+</sup> , Tl <sup>+</sup>	PME	[128]
Zn <sup>2+</sup> -2	1,13-Diaza-2,3;11,12;15,18-tribenzo-4,7,10-trioxacyclononaoctane-14,19-dione	30.0	$9.0 \times 10^{-5}$ - $10^{-1}$	$5.0 \times 10^{-5}$	K <sup>+</sup> , Na <sup>+</sup> , Li <sup>+</sup>	PME	[129]
Zn <sup>2+</sup> -3	5,6,14,15-Dibenzo-1,4-dioxa-8, 12-diazacyclopentadecane-5,14-diene	22.0	$5.0 \times 10^{-5}$ - $10^{-1}$	$3.0 \times 10^{-5}$	Ag <sup>+</sup> , Cu <sup>2+</sup> , Cd <sup>2+</sup>	PME	[130]
Zn <sup>2+</sup> -4	Tetra(2-aminophenyl) porphyrin	26.5	$5.0 \times 10^{-5}$ - $10^{-1}$	$3.0 \times 10^{-5}$	Ni <sup>2+</sup>	PME	[131]
Zn <sup>2+</sup> -5	Bis(2-nitrophenyl)disulfide	29.9	$2.9 \times 10^{-7}$ - $3.2 \times 10^{-2}$	$2.0 \times 10^{-7}$	Li <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup> , Pb <sup>2+</sup> , Cr <sup>3+</sup>	PME	[132]
Zn <sup>2+</sup> -6	3-[(2-Furylmethylene)amino]-2-thioxo-1,3-thiazolidin-4-one	29.3	$10^{-6}$ - $10^{-2}$	$8.5 \times 10^{-7}$	-	PME	[133]
Zn <sup>2+</sup> -7	5,6-Benzo-4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacos-5-ene	29.1	$10^{-6}$ - $10^{-1}$	$6.3 \times 10^{-7}$	-	PME	[134]
Cd <sup>2+</sup> -1	[1,1'-Bicyclohexyl]-1,1',2,2'-tetrol	27.8	$10^{-5}$ - $10^{-1}$	$9.0 \times 10^{-6}$	-	PME	[135]
Cd <sup>2+</sup> -2	Tetrathia-12-crown-4	29.0	$4.0 \times 10^{-7}$ - $10^{-1}$	$1.0 \times 10^{-7}$	Ag <sup>+</sup> , Tl <sup>+</sup> , Pb <sup>2+</sup> , K <sup>+</sup>	PME	[136]
Cd <sup>2+</sup> -3	5-[((4-Methyl phenyl) azo)-N-(6-amino-2-pyridin) salicylaldimine] and 5-[((4-methyl phenyl) azo)-N-(2-diamino-2-cyano-1-ethyl cyanide) salicylaldehyde]	28.0	$7.5 \times 10^{-7}$ - $1.5 \times 10^{-1}$	$7.5 \times 10^{-7}$	Pb <sup>2+</sup> , Ni <sup>2+</sup>	PME	[137]
		22.0	$4.0 \times 10^{-7}$ - $2.0 \times 10^{-1}$	$4.0 \times 10^{-7}$			
Cd <sup>2+</sup> -4	N'-[1-(2-Furyl)methylidene]-2-furohydrazide	29.4	$10^{-6}$ - $10^{-1}$	$7.3 \times 10^{-7}$	-	PME	[138]
Hg <sup>2+</sup> -1	Hexathia-18-crown-6-tetraone	29.0	$4.0 \times 10^{-6}$ - $10^{-3}$	$1.3 \times 10^{-6}$	Tl <sup>+</sup> , Ag <sup>+</sup>	PME	[139]
Hg <sup>2+</sup> -2	Dibenzodiazathia-18-crown-6-dione	29.0	$8.0 \times 10^{-6}$ - $10^{-2}$	$6.0 \times 10^{-6}$	Ag <sup>+</sup> , Pb <sup>2+</sup> , Cd <sup>2+</sup>	PME	[140]

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**Table 1.** Continued

Hg <sup>2+</sup> -3	2-Mercaptobenzimidazole, 2-mercaptopbenzothiazole and hexathiacyclooctadecane	28.5 28.5 29.6	10 <sup>-5</sup> -10 <sup>-1</sup> 10 <sup>-6</sup> -10 <sup>-1</sup> 10 <sup>-5</sup> -10 <sup>-1</sup>	6.0×10 <sup>-7</sup>	Ag <sup>+</sup> , NH <sub>4</sub> <sup>+</sup> , Ba <sup>2+</sup> , Pb <sup>2+</sup>	PME	[141]
Hg <sup>2+</sup> -4	Bis[5-((4-nitrophenyl)azo salicylaldehyde)]	30.0	7.0×10 <sup>-7</sup> -5.0×10 <sup>-2</sup>	2.0×10 <sup>-7</sup>	-	PME	[142]
Hg <sup>2+</sup> -5	2-Benzoylamino-3-(4-chloro- phenyl)-thioacrylic acid S-(2- mercapto-4-methyl-phenyl) ester	29.0	2.0×10 <sup>-7</sup> -3.0×10 <sup>-2</sup>	5.0×10 <sup>-8</sup>	Ni <sup>2+</sup>	PME	[143]
La <sup>3+</sup> -1	1,3,5-Trithiacyclohexane	19.8	8.0×10 <sup>-6</sup> -5.0×10 <sup>-2</sup> 4.0×10 <sup>-8</sup> -10 <sup>-2</sup>	5.0×10 <sup>-6</sup> 2.0×10 <sup>-8</sup>	-	PME CGE	[144]
La <sup>3+</sup> -2	N-[Hexahydrocyclopentapyrrol- 2((1H)yl)amino]carbonyl]-4- methyl benzene sulfonamide	20.1	10 <sup>-6</sup> -10 <sup>-1</sup>	8.0×10 <sup>-7</sup>	Sm <sup>3+</sup> , Ce <sup>3+</sup>	PME	[145]
La <sup>3+</sup> -3	Bis(2-mercaptoanil) diacetyl	19.7	10 <sup>-5</sup> -10 <sup>-1</sup> 10 <sup>-6</sup> -10 <sup>-1</sup>	6.5×10 <sup>-6</sup> 5.0×10 <sup>-7</sup>	Ce <sup>3+</sup> , Gd <sup>3+</sup>	PME CGE	[146]
La <sup>3+</sup> -4	Bis(thiophenol)phenylen-1,3- diamine	19.6	10 <sup>-7</sup> -10 <sup>-1</sup>	2.0×10 <sup>-8</sup>	Sm <sup>3+</sup> , Ce <sup>3+</sup>	PME	[147]
La <sup>3+</sup> -5	2,2'-Dithiodipyridine	20.0	7.1×10 <sup>-6</sup> -2.2×10 <sup>-2</sup>	3.1×10 <sup>-6</sup>	Pb <sup>2+</sup> , Ce <sup>3+</sup>	PME	[148]
La <sup>3+</sup> -6	N-2,4-Dimethylphenyl-N'- ethylformamidine	19.8	10 <sup>-7</sup> -10 <sup>-1</sup>	8.0×10 <sup>-8</sup>	-	PME	[149]
La <sup>3+</sup> -7	Bis(2-methylbenzaldehyde) butane-2,3-dihydrazone	19.8	10 <sup>-5</sup> -10 <sup>-1</sup>	7.0×10 <sup>-6</sup>	Ce <sup>3+</sup> , Pr <sup>3+</sup> , Eu <sup>3+</sup>	PME	[150]
La <sup>3+</sup> -8	N,N'-Adipylbis(5-plenylazo salicylaldehyde hydrazone)	19.4	10 <sup>-6</sup> -10 <sup>-2</sup>	4.0×10 <sup>-7</sup>	Yb	PME	[151]
La <sup>3+</sup> -9	Bis(5-nitro-2-furaldehyde)butane- 2,3-dihydrazone	19.8	10 <sup>-7</sup> -10 <sup>-1</sup>	4.0×10 <sup>-8</sup>	-	PME	[152]
La <sup>3+</sup> -10	N-(2-Pyridyl)-N'-(4-methoxy- phenyl)-thiourea	19.6	4.0×10 <sup>-8</sup> -10 <sup>-1</sup>	2.0×10 <sup>-8</sup>	Pr <sup>3+</sup> , Ce <sup>3+</sup>	PME	[153]
La <sup>3+</sup> -11	4-Methyl-2-hydrazino-benzo- thiazole	19.8	10 <sup>-7</sup> -10 <sup>-1</sup>	2.5×10 <sup>-8</sup>	Ce <sup>3+</sup>	PME	[154]
La <sup>3+</sup> -12	8-Amino-N-(2-hydroxy- benzylidene) naphthylamine	20.3	10 <sup>-7</sup> -10 <sup>-1</sup>	8.0×10 <sup>-8</sup>	Pr <sup>3+</sup>	PME	[155]
La <sup>3+</sup> -13	3-Hydroxy-N'-(pyridin-2- ylmethylen)-2-naphthohydrazide	19.2	10 <sup>-7</sup> -10 <sup>-2</sup>	7.0×10 <sup>-8</sup>	-	PME	[156]
La <sup>3+</sup> -14	N'-(1-Pyridin-2-ylmethylene)-2- furohydrazide	19.2	10 <sup>-6</sup> -10 <sup>-1</sup>	7.0×10 <sup>-7</sup>	Sm <sup>3+</sup> , Nd <sup>3+</sup> , Dy <sup>3+</sup>	PME	[157]
Ce <sup>3+</sup> -1	1,3,5-Trithiane	19.2	2.5×10 <sup>-8</sup> -4.8×10 <sup>-4</sup>	2.0×10 <sup>-8</sup>	La <sup>3+</sup> , Pb <sup>2+</sup>	GCE	[158]

**Table 1.** Continued

Ce <sup>3+</sup> -2	1,3,5-Trithiane	19.4	5.0×10 <sup>-5</sup> -10 <sup>-1</sup>	3.0×10 <sup>-5</sup>	Cd <sup>3+</sup> , Zn <sup>2+</sup> , La <sup>3+</sup>	PME	[159]
Ce <sup>3+</sup> -3	N-[{(Z)-2-Chloro-2-(1-hydroxy-1,1,1-triphenyl phosphoranyl)-1-ethenyl]-4-ethyl-1-benzene sulfonamide}	19.5	6.6×10 <sup>-7</sup> -6.2×10 <sup>-2</sup>	2.3×10 <sup>-7</sup>	La <sup>3+</sup> , Sm <sup>3+</sup>	PME	[160]
Ce <sup>3+</sup> -4	2-Aminobenzothiazole	19.6	2.0×10 <sup>-6</sup> -2.0×10 <sup>-2</sup>	1.8×10 <sup>-6</sup>	La <sup>3+</sup> , Al <sup>3+</sup> , Fe <sup>2+</sup>	PME	[161]
Ce <sup>3+</sup> -5	N'-(2-Hydroxyphenyl)methylidene]-2-furohydrazide	19.4	10 <sup>-5</sup> -10 <sup>-2</sup>	7.6×10 <sup>-6</sup>	-	PME	[162]
Pr <sup>3+</sup>	N'-(Pyridin-2-ylmethylene) benzo-hydrazide	21.1	10-6-10 <sup>-2</sup>	8.0×10 <sup>-7</sup>	Er <sup>3+</sup> , Sm <sup>3+</sup> , Lu <sup>3+</sup>	PME	[163]
Nd <sup>3+</sup> -1	5-Pyridino-2,8-dithia[9](2,9)-1,10-phenanthroline-phane	20.1	10-6-10 <sup>-2</sup>	7.9×10 <sup>-7</sup>	Yb <sup>3+</sup> , Ce <sup>3+</sup> , Gd <sup>3+</sup>	PME	[164]
Nd <sup>3+</sup> -2	N-(2-Furylmethylene) pyridine-2,6-diamine	19.6	10 <sup>-5</sup> -10 <sup>-2</sup>	7.0×10 <sup>-6</sup>	La <sup>3+</sup> , Gd <sup>3+</sup> , Sm <sup>3+</sup>	PME	[165]
Nd <sup>3+</sup> -3	2-{[(6-Aminopyridin-2-yl)imino]methyl}-phenol	19.6	10 <sup>-5</sup> -10 <sup>-2</sup>	2.0×10 <sup>-6</sup>	Gd <sup>3+</sup> , La <sup>3+</sup> , Sm <sup>3+</sup>	PME	[166]
Sm <sup>3+</sup> -1	4,5,6,7-Tetrathiocino[1,2-b:3,4-b']diimidazolyl-1,3,8,10-tetraethyl-2,9-dithione (Et(4)todit)	19.6	10 <sup>-5</sup> -10 <sup>-1</sup> 10 <sup>-7</sup> -10 <sup>-1</sup>	8.0×10 <sup>-6</sup> 1.6×10 <sup>-8</sup>	Pb <sup>2+</sup> , Ce <sup>3+</sup> , Gd <sup>3+</sup>	PME CGE	[167]
Sm <sup>3+</sup> -2	Isopropyl 2-[(isopropoxy-carbothioyl) disulfanyl] ethanethioate	19.2	10 <sup>-5</sup> -10 <sup>-1</sup> 10 <sup>-6</sup> -10 <sup>-1</sup>	3.1×10 <sup>-6</sup> 5.0×10 <sup>-7</sup>	Gd <sup>3+</sup> , Cd <sup>3+</sup> , Hg <sup>2+</sup>	PME CGE	[168]
Sm <sup>3+</sup> -3	N-[2-[4-[[[(Cyclohexylamino)carbonyl] anilino] sulfonyl]phenyl]ethyl]-5-methyl pyrazine carboxamide	19.8	10 <sup>-6</sup> -10 <sup>-1</sup>	6.7×10 <sup>-7</sup>	Ag <sup>+</sup> , Pb <sup>2+</sup> , Ce <sup>3+</sup>	PME	[169]
Sm <sup>3+</sup> -4	N-[2-[4-[[[(Cyclohexylamino)carbonyl] amino] sulfonyl] phenyl]ethyl]-5-methyl pyrazine carboxamide	19.3	10 <sup>-10</sup> -10 <sup>-5</sup>	8.0×10 <sup>-11</sup>	-	CGE	[170]
Eu <sup>3+</sup> -1	N,N-Diethyl-N-(4-hydroxy-6-methylpyridin-2-yl)guanidine	19.8	7.0×10 <sup>-5</sup> - 10 <sup>-1</sup>	7.0×10 <sup>-5</sup>	Gd <sup>3+</sup> , Ce <sup>3+</sup> , Tb <sup>3+</sup>	PME	[171]
Eu <sup>3+</sup> -2	Bis(thiophenol)butane2,3-dihydrazone	19.8	10 <sup>-5</sup> -10 <sup>-2</sup>	5.0×10 <sup>-6</sup>	La <sup>3+</sup> , Gd <sup>3+</sup> , Sm <sup>3+</sup>	PME	[172]
Gd <sup>3+</sup> -1	(2-[{3-[(2-Sulfanylphenyl)imino]-1-methylbutylidene}amino]phenyl hydrosulfide	19.8	10 <sup>-5</sup> -10 <sup>-1</sup>	3.0×10 <sup>-6</sup>	Tb <sup>3+</sup> , Dy <sup>3+</sup> , Eu <sup>3+</sup>	PME	[173]
Gd <sup>3+</sup> -2	Omeprazole	19.3	10 <sup>-5</sup> -10 <sup>-1</sup>	5.0×10 <sup>-6</sup>	Ce <sup>3+</sup> , Cd <sup>2+</sup>	PME	[174]

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**Table 1.** Continued

Gd <sup>3+</sup> -3	Bis(thiophenal) pyridine-2,6-diamine	19.4	10 <sup>-6</sup> -10 <sup>-1</sup>	7.0×10 <sup>-7</sup>	La <sup>3+</sup> , Sm <sup>3+</sup>	PME	[175]
Gd <sup>3+</sup> -4	N-(2-Pyridyl)-N'-(4-nitrophenyl) thiourea	19.95	3.0×10 <sup>-7</sup> -10 <sup>-1</sup>	3.0×10 <sup>-7</sup>	-	PME	[176]
Tb <sup>3+</sup> -1	N,N-Bis(pyrrolidene) benzene-1,2-diamine	19.8	10 <sup>-5</sup> -10 <sup>-1</sup>	7.0×10 <sup>-6</sup>	Yb <sup>3+</sup> , Sm <sup>3+</sup> , Dy <sup>3+</sup>	PME	[177]
Tb <sup>3+</sup> -2	4-Amino-3-{2-[4-amino-6-methyl-5-oxo-4,5-dihydro-1,2,4-triazin-3(2H)-yliden]hydrazone}-6-methyl-3,4-dihydro-1,2,4-triazin-5(2H)-one	19.4	10 <sup>-6</sup> -10 <sup>-1</sup>	8.6×10 <sup>-7</sup>	Gd <sup>3+</sup>	PME	[178]
Dy <sup>3+</sup> -1	N,N-Bis(pyrrolidene) benzene-1,2-diamine, poly(vinyl chloride)	20.6	10 <sup>-5</sup> -10 <sup>-1</sup>	6.0×10 <sup>-6</sup>	Ce <sup>3+</sup> , La <sup>3+</sup>	PME	[179]
Dy <sup>3+</sup> -2	[(E)-N-(2-Hydroxybenzylidene) benzohydraide]	20.1	10 <sup>-6</sup> -10 <sup>-2</sup>	8.0×10 <sup>-7</sup>	Yb <sup>3+</sup>	PME	[180]
Ho <sup>3+</sup> -1	N,N'-Bis(2-pyridinecarboxamide)-1,2-benzene	19.6	10 <sup>-5</sup> -10 <sup>-2</sup>	8.0×10 <sup>-6</sup>	Dy <sup>3+</sup> , Sm <sup>3+</sup> , Er <sup>3+</sup>	PME	[181]
Ho <sup>3+</sup> -2	N-(1-Thien-2-ylmethylene)-1,3-benzothiazol-2-amine	19.7	10 <sup>-5</sup> -10 <sup>-2</sup>	7.0×10 <sup>-6</sup>	Dy <sup>3+</sup> , Gd <sup>3+</sup> , Lu <sup>3+</sup>	PME	[182]
Er <sup>3+</sup>	N'-(2-Hydroxy-1,2-diphenyl-ethylidene) benzohydrazide	21.0	10 <sup>-7</sup> -10 <sup>-2</sup>	7.0×10 <sup>-8</sup>	-	PME	[183]
Tm <sup>3+</sup> -1	Thiophene-2-carbaldehyde-(7-methyl-1,3-benzothiazol-2-yl)hydrazone	19.5	10 <sup>-5</sup> -10 <sup>-2</sup>	8.0×10 <sup>-6</sup>	Nd <sup>3+</sup> , Ho <sup>3+</sup> , Er <sup>3+</sup>	PME	[184]
Tm <sup>3+</sup> -2	2,2'-Dianiline disulfide	19.5	10 <sup>-6</sup> -10 <sup>-2</sup>	4.0×10 <sup>-7</sup>	Yb <sup>3+</sup> , Pr <sup>3+</sup> , Lu <sup>3+</sup>	PME	[185]
Yb <sup>3+</sup> -1	Cefixime	19.5	10 <sup>-6</sup> -10 <sup>-2</sup>	7.0×10 <sup>-7</sup>	Ce <sup>3+</sup> , Cu <sup>3+</sup>	PME	[186]
Yb <sup>3+</sup> -2	N-(2-Pyridyl)-N'-(2methoxyphenyl)-thiourea	19.3	10 <sup>-6</sup> -10 <sup>-2</sup>	5.0×10 <sup>-7</sup>	Dy <sup>3+</sup> , Gd <sup>3+</sup> , Nd <sup>3+</sup>	PME	[187]
Yb <sup>3+</sup> -3	3-Hydroxy-N-[(2-hydroxyphenyl)methylene]-2-naphthohydrazide	19.2	10 <sup>-7</sup> -10 <sup>-2</sup>	4.0×10 <sup>-8</sup>	Gd <sup>3+</sup> , Nd <sup>3+</sup>	PME	[188]
Lu <sup>3+</sup>	N-(Thien-2-ylmethylene)pyridine-2,6-diamine	20.5	10 <sup>-6</sup> -10 <sup>-2</sup>	8.0×10 <sup>-7</sup>	Nd <sup>3+</sup>	PME	[189]
UO <sub>2</sub> <sup>2+</sup> -1	1,18-Diaza-3,4,15,16-dibenzo-5,8,11,14,21,24-hexaoxacyclohexaeicosane-2,17-dione	29.8	3.0×10 <sup>-6</sup> -8.2×10 <sup>-3</sup> 5.0×10 <sup>-7</sup> -1.5×10 <sup>-3</sup>	2.2×10 <sup>-6</sup> 1.5×10 <sup>-7</sup>	K <sup>+</sup> , NH <sub>4</sub> <sup>+</sup> , Mn <sup>2+</sup> , Ni <sup>2+</sup>	PME CGE	[190]
UO <sub>2</sub> <sup>2+</sup> -2	2,2'-[1,2-Ethandiyil bis(nitriloethylidene)]bis(1-naphthalene)	28.5	10 <sup>-7</sup> -10 <sup>-1</sup>	7.0×10 <sup>-8</sup>	Mg <sup>2+</sup> , Cu <sup>2+</sup>	PME	[191]

diamine [82], and a mercapto compound [83]. The minimum detection limit among these  $\text{Ni}^{2+}$  sensors was  $6.0 \times 10^{-8} \text{ M}$  [75-83].

The highest sensitivity was observed in the case of a 1,3,7,9,13,15,19,21-octazapentacyclooctacosane (penta cyclooctaaza) based  $\text{Ni}^{2+}$  sensor showing a slope of  $30.5 \text{ mV dec}^{-1}$  of concentration [81].

The only  $\text{Pd}^{2+}$  sensor (hexadecylpyridinium cation-based) was designed in the form of both a polymeric membrane electropode PME ( $\text{DL} = 1.0 \times 10^{-6}$ ), and a coated wire electrode (CWE) ( $\text{DL} = 5.0 \times 10^{-8}$ ). This sensor showed a good selectivity behavior and suffered interferences only from  $\text{Pt}^{2+}$  [84].

The detection limits of the  $\text{Co}^{2+}$  sensors which were based on 18-membered macrocyclic diamide [85], (2-mercaptop-4-methylphenyl)-2-benzamido-3-phenyl-thiopropenoate [86], dibenzopyridino-substituted macrocyclic diamide 5-((4-nitrophenyl)azo)-N-(2',4'-dimethoxy phenyl) salicylaldimine [88] and oxime of 1-(2-oxocyclohexyl)-1,2-cyclohexanediol [87] as the ionophores were in the range of  $10^{-7}$ - $10^{-6} \text{ M}$  and they showed almost Nernstian potential slopes [85-89].

Numerous  $\text{Cu}^{2+}$  sensors have been constructed by Iranian scientists including CGEs [94,98], CWEs [99,104,111], sol-gel electrode [105] and mostly PMEs [90-112]. Almost all of these sensors have Nernstian behaviors and the minimum detection limit is reported in the case of a 2-{1-(E)-2-((Z)-2-[(E)-2-[(Z)-1-(2-hydroxyphenyl) ethylidene] hydrazono]-1-methylpropylidene) hydrazono}ethylphenol based PME [110].

A large number of  $\text{Ag}^+$  sensors based on hexathia-18-crown-6 [113], mixed aza-thioether crowns containing a 1,10-phenanthroline sub-unit, 2-mercaptopbenzimidazole [114,115], 2-mercaptopbenzothiazole [116], 2,c-8,c-14,c-20-tetrabutyl-4,6,10, 12,16,18,22,24-octaacetyl-resorc[4]arene [117], thia-substituted macrocyclic diamide [118], C-methylcalix[4]resorcareneocta-methyl ester [119], methyl-2-pyridyl ketone oxime [120], phenyl-2-pyridyl ketone oxime [120] and bis[2-(*o*-carboxythiophenoxy) methyl]-4-bromo-1-methoxybenzene [120], octahydroxycalix [4]arene derivative meso-tetraphenylporphine [ $\text{H}_2\text{T}(4-\text{OCH}_3)\text{PP}$ ] [121,122], 2-[(2-{2-[(2-carboxyphenyl)sulfanyl]ethoxy} ethyl) sulfanyl] benzoic acid [123], N,N'-bis(2-thienylmethylene)-1,2-diaminobenzene [124], cone shaped calix[4]arene [125], 2-

methyl-2,4-di(2-thienyl)-2,3-dihydro-1H-1,5-benzodiazepine [126], [bis 5-(4-nitrophenyl azo) salisylaldimine]-1,8-diamino [127], 3,6-dioxooctane have been constructed [113-127]. The major interferences in the case of these sensors are caused by  $\text{Ti}^{4+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Fe}^{3+}$ , and the minimum detection limit among the is reported to be around  $1.2 \times 10^{-8} \text{ M}$  [123].

Cryptand C<sub>2</sub>B22 [128], 1,13-diaza-2,3;11,12;15,18-tribenzo-4,7,10-trioxacyclononaoctane-14,19-dione [129], 5,6,14,15-dibenzo-1,4-dioxa-8,12-diazacyclopentadecane-5,14-diene [130], tetra(2-aminophenyl) porphyrin [131], bis(2-nitrophenyl) disulfide [132], 3-[(2-furylmethylene)amino]-2-thioxo-1,3-thiazolidin-4-one [133] and 5,6-benzo-4,7,13,16,21, 24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacos-5-ene [134] have been used in the construction of PMEs for  $\text{Zn}^{2+}$  ions [128-134], three of which showed sub-Nernstian responses [128,130,131]. The lowest detection limit reported for a  $\text{Zn}^{2+}$  sensor was  $2 \times 10^{-7} \text{ M}$  [132].

Other transition metal ion selective electrodes include [1,1'-bicyclohexyl]-1,1',2,2'-tetrol [135], tetrathia-12-crown-4 [136], 5-[((4-methylphenyl)azo)-N-(6-amino-2-pyridin) salicylaldimine] [137] and 5-[((4-methylphenyl)azo)-N-(2-diamino-2-cyano-1-ethyl cyanide) salicylaldehyde] [137], and N'-[1-(2-furyl)methylidene]-2-furohydrazide based PMEs for  $\text{Cd}^{2+}$  [135-138] and  $\text{Hg}^{2+}$  ions [139-143].

There have also been several reports by Iranian researchers on ion selective sensors for lanthanide and actinide ions including 14  $\text{La}^{3+}$  sensors that are mostly PMEs [144-157]. The reports also encompass 1,3,5-trithiane, N-[(Z)-2-chloro-2-(1-hydroxy-1,1,1-triphenyl phosphoranyl)-1-ethenyl]-4-ethyl-1-benzene sulfonamide, 2-aminobenzothiazole, N'-[(2-hydroxyphenyl)methylidene]-2-furohydrazide based cerium sensors [158-162].

Only  $\text{Pr}^{3+}$  sensor based on N'-(pyridin-2-ylmethylene) benzohydrazide, sensor with a slope of  $21.1 \text{ mV dec}^{-1}$  of concentration and a detection limit of  $8.0 \times 10^{-7} \text{ M}$  has been developed, the major interfering ions of which are  $\text{Er}^{3+}$ ,  $\text{Sm}^{3+}$  [163].

The other sensors in this group include  $\text{Nd}^{3+}$  PMEs [164-166], with major interfering ions of  $\text{Yb}^{3+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{La}^{3+}$ ,  $\text{Sm}^{3+}$ , and the minimum detection limit of  $7.9 \times 10^{-7} \text{ M}$ . There have also been reports on  $\text{Sm}^{3+}$  sensors based on ionophores with N, and S donor atoms like the other lanthanide and

transition metal ion sensors. These  $\text{Sm}^{3+}$  sensors [167-170], are mostly CGEs and PMEs and the minimum detection limit is reported to be  $8.0 \times 10^{-11} \text{ M}$  [170].

Other sensors include  $\text{Eu}^{3+}$  [171,172],  $\text{Gd}^{3+}$  [173-176],  $\text{Tb}^{3+}$  [177,178],  $\text{Dy}^{3+}$  [179,180],  $\text{Ho}^{3+}$  [181,182],  $\text{Er}^{3+}$  [183],  $\text{Tm}^{3+}$  [184,185],  $\text{Yb}^{3+}$  [186-188] PMEs, in addition to one  $\text{Lu}^{3+}$  PME [189] and two uranyl PMEs and GCE [190,191]. The minimum detection limit among all of these sensors is reported to be  $7.0 \times 10^{-8} \text{ M}$  for uranyl ion [191], which is a 2,2'-[1,2-ethandiylbis (nitriloethylidene)]bis(1-naphthalene) based  $\text{UO}_2^{2+}$  polymeric membrane sensor with a composition of PVC:diocetylphthalatesionophore:sodium tetraphenylborate percent ratio of 30.5:63.5:4.0:2.0.

## ANION SELECTIVE ELECTRODES

Anion selective electrodes, just like cation selective ones, are an important group of ion selective electrodes. The number of an ion selective electrodes is lower than that of the cationic sensors, due to reasons like the relative larger size of anions, their various shapes, and their high hydration energies; however, there have been a relatively large number of sensors for anionic species by Iranian researchers during the past decade.

$\text{NO}_3^-$  CWE and PMEs [192-194] and  $\text{NO}_2^-$  CGE and PMEs [195-197] have been designed, which overall, suffer from  $\text{ClO}_4^-$ ,  $\text{ClO}_3^-$ , salicylate,  $\text{I}^-$ , and  $\text{SCN}^-$  interferences. The lowest detection limit among these sensors belongs to a derivative of (tetraphenylporphyrinato)cobalt(III) acetate based CGE and is about  $2.0 \times 10^{-8} \text{ M}$  [195].

The  $\text{HPO}_4^{2-}$  sensors that have been reported were based on vanadyl [198,199] and molybdenum [200,201] complexes and showed almost Nernstian potential slopes.

There have been quite a lot reports on PMEs [202-217] and a few CGEs [208,212] for  $\text{SCN}^-$  ion. These sensors have been based on different complexes, as well as 1,8-dibenzyl-1,3,6,8,10,13-hexaaazacyclotetradecane [210]. The major interfering ions include  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $\text{SCN}^-$ ,  $\text{ClO}_4^-$ , salicylate,  $\text{MnO}_4^-$ , and the least detection limit was reported to be  $4.8 \times 10^{-8} \text{ M}$  [208].  $\text{SO}_4^{2-}$  sensors have also been reported based on different complexes of zinc [218,223,224] and nickel [219-222,225-229], and also some pyrylium derivatives [219-221,225-229]. The minimum detection limit was found to be

in the range of  $1.0 \times 10^{-8} \text{ M}$ . However, the best sensor for this anion was reported to have a composition of 30% PVC, 61% Nitophenoxyoctyl ether, 5% ionophore, 4% Hexadecyltrimethylammonium bromide [225].

Sensors for the lipophilic  $\text{ClO}_4^-$  have also been constructed based on Ni(II)-hexaaazacyclotetradecane [230], phosphorus(V)-tetraphenylporphyrin [231], cobaloxime [232], 1,3,5,8,10,13-hexa-azacyclotetradecane [233], 1,8-tert-butyl-1,3,5,8,10,13-hexa-azacyclotetradecane [233], and two nickel-hexaazamacrocycles [234]. The only  $\text{Cl}^-$  sensor was based on a thallium(III) Schiff's base [245] with no considerable interferences, which had a detection limit of  $2.0 \times 10^{-6} \text{ M}$ . The other halogen sensors include  $\text{Br}^-$  ion PMEs [246-248], based on 14-phenyldibenzo[a]xantheniumbromide [236], bis(4-hydroxyphenyl)-1,4-diaza-1,3-butadiene-Hg(II) [237], iron(III)-salen [238], which suffer interferences only from  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{I}^-$ ,  $\text{SCN}^-$ . Iodine sensors were more in number [249-248], and have been mostly PMEs, although they include some CGEs. The sensors had detection limits in the range of  $10^{-7}$ - $10^{-5} \text{ M}$ , the lowest among which was reported to be  $3 \times 10^{-7} \text{ M}$  [248].

There have been reports on triiodide anion, based on 2,4,6,8-tetraphenyl-2,4,6,8-tetraazabicyclo[3.3.0]octane [249], tetra(*p*-chlorophenyl) porphyrinatomanganese(III) acetate [250], ketoconazole-triiodide ion pair [251], charge-transfer complexes and amino crown ether [252], complexes of Schiff base 2,2'[4,4'-diphenylmethane bis(nitromethylidyne)] bisphenol [253], iodine charge-transfer complex and bis(2-hydroxyacetophenone)butane-2,3-dihydrazone [254], 7,16-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane [255], mercury-salen [256], copper (II)-Schiff base [257], charge-transfer complex of bis(2,4-dimethoxybenzaldehyde)butane-2,3-dihydrazone with iodine, 2-(((2-((E)-1-(2-hydroxyphenyl)methylidyne) amino) phenyl) imino) methyl phenol [258,259], N,N'-1,2-propylene-bis-(5-methyl salicylidene iminato) copper [260], bis(2-hydroxybenzophenone) butane-2,3-dihydrazone as the ionophores.

There have also been some reports on  $\text{CrO}_4^{2-}$  CWEs based on nickel, cobalt, manganese, copper, zinc, and rhodium bis(acetylacetone)copper(II) [262], bis(acetylacetone) cadmium(II) [263], with detection limits of about  $1.0 \times 10^{-6} \text{ M}$  and interferences only from  $\text{I}^-$  and  $\text{ClO}_4^-$ . The only  $\text{MoO}_4^{2-}$  sensor was based on cerium phosphate [264]. In Table 2 are

**Table 2.** Anionic Sensors Published by the Iranian Researchers in the Past Decade

Anion	Ionophore	Slope	LR (M)	DL (M)	Anion with $\log K_{Sel} > -2$	TS	Ref.
$\text{NO}_3^-$ -1	Bis(2-hydroxyanil)acetylacetone lead(II)	-58.8	$2.0 \times 10^{-5}$ - $1.0 \times 10^{-1}$	$1.0 \times 10^{-6}$	$\text{ClO}_4^-$ , $\text{ClO}_3^-$ , Salicylate	PME	[192]
$\text{NO}_3^-$ -2	Bis(2-hydroxyacetophenone ethylenedimine vanadyl(IV))	-58.5	$5.0 \times 10^{-6}$ -1	$1.0 \times 10^{-6}$	Salicylate, I <sup>-</sup> , SCN <sup>-</sup>	PME	[193]
$\text{NO}_3^-$ -3	Tetramethyl cyclotetra-decanato-nickel(II) complex	-57.8	$10^{-5}$ -1	$5.0 \times 10^{-6}$	$\text{ClO}_4^-$ , SCN <sup>-</sup> , I <sup>-</sup>	CWE	[194]
$\text{NO}_2^-$ -1	Derivatives of (Tetraphenylporphyrinato) cobalt(III) acetate	-60.3	$10^{-6}$ - $10^{-1}$	$8.0 \times 10^{-7}$	SCN <sup>-</sup>	PME	[195]
		-60.3	$5.0 \times 10^{-8}$ - $5.0 \times 10^{-2}$	$2.0 \times 10^{-8}$		CGE	
$\text{NO}_2^-$ -2	Cobalt(II)-salen	-58.2	$10^{-6}$ - $10^{-1}$	$5.0 \times 10^{-7}$	-	PME	[196]
$\text{NO}_2^-$ -3	Cobalt(II) salophen	-59.8	$10^{-6}$ - $10^{-1}$	$8.0 \times 10^{-7}$	-	PME	[197]
$\text{HPO}_4^{2-}$ -1	Vanadyl salophen	-24.3	$10^{-6}$ - $10^{-1}$	$5.0 \times 10^{-7}$	-	PME	[198]
$\text{HPO}_4^{2-}$ -2	Vanadyl salen	-28.8	$5.0 \times 10^{-6}$ - $10^{-1}$	$3.0 \times 10^{-6}$	-	PME	[199]
$\text{HPO}_4^{2-}$ -3	Molybdenum bis(2-hydroxyanil) acetylacetone	-29.5	$10^{-7}$ - $10^{-1}$	$6.0 \times 10^{-8}$	-	PME	[200]
$\text{HPO}_4^{2-}$ -4	Oxo-molybdenum methyl-salen	-28.6	$4.0 \times 10^{-7}$ - $10^{-1}$	$2.0 \times 10^{-7}$	-	PME	[201]
$\text{SCN}^-$ -1	(Octabromotetraphenyl porphyrinato)manganese(III) chloride	-58.3	$4.8 \times 10^{-7}$ -1	$3.2 \times 10^{-7}$	$\text{N}_3^-$ , I <sup>-</sup> , Br <sup>-</sup>	PME	[202]
$\text{SCN}^-$ -2	Nickel and iron phthalocyanines	-58.4	$5.0 \times 10^{-7}$ - $10^{-1}$	$5.0 \times 10^{-7}$	SCN <sup>-</sup> , $\text{ClO}_4^-$ , I <sup>-</sup>	CGE	[203]
$\text{SCN}^-$ -3	Cobalt and manganese phthalocyanine	-59.0	$10^{-6}$ - $10^{-1}$	$5.0 \times 10^{-7}$	I <sup>-</sup> , CN <sup>-</sup>	CGE	[204]
$\text{SCN}^-$ -4	Copper-1,8-dimethyl-1,3,6,8,10, 13-azacyclotetradecane	57.2	$7.0 \times 10^{-6}$ - $10^{-1}$	$4.0 \times 10^{-6}$	$\text{ClO}_4^-$ , CN <sup>-</sup>	PME	[205]
$\text{SCN}^-$ -5	Manganese porphyrin derivatives	59.5	$5.0 \times 10^{-7}$ - $10^{-1}$	$5.0 \times 10^{-8}$	SCN <sup>-</sup> , $\text{ClO}_4^-$ , Salicylate	PME	[206]
$\text{SCN}^-$ -6	Cadmium salen	59.1	$10^{-6}$ - $10^{-1}$	$7.0 \times 10^{-7}$	$\text{MnO}_4^-$ , I <sup>-</sup>	PME	[207]
$\text{SCN}^-$ -7	Nickel(II)-azamacrocyclic complex	-57.8	$10^{-7}$ - $10^{-1}$	$4.8 \times 10^{-8}$	-	CGE	[208]
$\text{SCN}^-$ -8	Unsymmetrical benzo N(4) nickel(H) macrocyclic complexes	-59.7	$1.4 \times 10^{-7}$ - $10^{-1}$	$1.4 \times 10^{-7}$	SCN <sup>-</sup> , $\text{ClO}_4^-$ , I <sup>-</sup>	PME	[209]
$\text{SCN}^-$ -9	1,8-Dibenzyl-1,3,6,8,10,13-hexa-azacyclotetradecane	-58.4	$3.3 \times 10^{-6}$ - $10^{-1}$	$3.0 \times 10^{-6}$	-	PME	[210]
$\text{SCN}^-$ -10	Bis(2-mercaptopbenzoxazolato) mercury(II) and bis(2-pyridinethiolato)mercury(II)	-60.6	$10^{-6}$ - $10^{-1}$	$6.0 \times 10^{-7}$	$\text{ClO}_4^-$ , Cl <sup>-</sup>	PME	[211]
		-57.5					

## One Decade of Research on Ion-Selective Electrodes in Iran

**Table 2.** Continued

SCN <sup>-</sup> -11	Cu(L)](NO <sub>3</sub> ) <sub>2</sub> (L = 4,7-bis(3-aminopropyl)-1-thia-4,7-diazacyclononane)	-57.6 -58.8	10 <sup>-6</sup> -10 <sup>-1</sup> 5.0×10 <sup>-7</sup> -10 <sup>-2</sup>	8.5×10 <sup>-7</sup> 8.0×10 <sup>-8</sup>	ClO <sub>4</sub> <sup>-</sup> , I <sup>-</sup> , Salicylate	PME CGE	[212]
SCN <sup>-</sup> -12	2,2-[(1,3-Dimethyl-1,3-propanediylidene)dinitrilo]bis-benzenethiolato cadmium(II)	-58.9	10 <sup>-6</sup> -10 <sup>-1</sup>	5.0×10 <sup>-7</sup>	MnO <sub>4</sub> <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup> , Br <sup>-</sup>	PME	[213]
SCN <sup>-</sup> -13	Butane-2,3-dione bis(salicyl-hydrazone)zinc(II)	-56.5	10 <sup>-6</sup> -10 <sup>-1</sup>	7.0×10 <sup>-7</sup>	ClO <sub>4</sub> <sup>-</sup>	PME	[214]
SCN <sup>-</sup> -14	Rh(III) complex	-58.7	10 <sup>-5</sup> -10 <sup>-1</sup>	4.0×10 <sup>-6</sup>	ClO <sub>4</sub> <sup>-</sup>	PME	[215]
SCN <sup>-</sup> -15	Rhodium(II) phthalocyanine	-56.3	10 <sup>-6</sup> -10 <sup>-1</sup>	7.9×10 <sup>-7</sup>	ClO <sub>4</sub> <sup>-</sup> , Salicylate, I <sup>-</sup>	PME	[216]
SCN <sup>-</sup> -16	Nickel(II)-1,4-,8,11,15,18,22,25-octabutoxyphthalocyanine	-58.7	10 <sup>-6</sup> -10 <sup>-1</sup>	5.7×10 <sup>-7</sup>	-	PME	[217]
SO <sub>4</sub> <sup>2-</sup> -1	Complex of Zn(II)	-29.7 -29.3	5.0×10 <sup>-5</sup> -10 <sup>-1</sup> 10 <sup>-7</sup> -10 <sup>-1</sup>	2.8×10 <sup>-5</sup> 8.5×10 <sup>-8</sup>	SCN <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup>	PME CGE	[218]
SO <sub>4</sub> <sup>2-</sup> -2	2,6-Dianisol-4-phenyl-pyrilium perchlorate	-28.8	10 <sup>-6</sup> -10 <sup>-1</sup>	8.0×10 <sup>-7</sup>	SO <sub>3</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup>	PME	[219]
SO <sub>4</sub> <sup>2-</sup> -3	Pyrilium perchlorate derivative	-28.9	10 <sup>-6</sup> -10 <sup>-1</sup>	8.0×10 <sup>-7</sup>	SO <sub>3</sub> <sup>2-</sup> , Br <sup>-</sup> , SCN <sup>-</sup>	PME	[220]
SO <sub>4</sub> <sup>2-</sup> -4	2,5-Diphenyl-1,2,4,5-tetraaza-bicyclo[2.2.1]heptane	-28.8	9.0×10 <sup>-6</sup> -10 <sup>-1</sup>	7.0×10 <sup>-6</sup>	SO <sub>3</sub> <sup>2-</sup> , I <sup>-</sup>	PME	[221]
SO <sub>4</sub> <sup>2-</sup> -5	Strontium Schiff's base	-29.2	10 <sup>-6</sup> -10 <sup>-2</sup>	5.0×10 <sup>-7</sup>	SO <sub>3</sub> <sup>2-</sup> , CO <sub>3</sub> <sup>2-</sup> , Cl <sup>-</sup>	PME	[222]
SO <sub>4</sub> <sup>2-</sup> -6	Zinc-phthalocyanine	-29.2	10 <sup>-6</sup> -10 <sup>-2</sup>	8.0×10 <sup>-7</sup>	SO <sub>3</sub> <sup>2-</sup> , CH <sub>3</sub> COO <sup>-</sup>	PME	[223]
SO <sub>4</sub> <sup>2-</sup> -7	Zinc-Schiff base	-29.2	10 <sup>-6</sup> -10 <sup>-2</sup>	9.0×10 <sup>-7</sup>	-	PME	[224]
SO <sub>4</sub> <sup>2-</sup> -8	Bis-pyrilium derivative	-29.5	10 <sup>-7</sup> -10 <sup>-1</sup>	5.0×10 <sup>-8</sup>	-	PME	[225]
SO <sub>4</sub> <sup>2-</sup> -9	2,6-Diphenylpyrylium fluoroborate	-29.5	5.0×10 <sup>-6</sup> -10 <sup>-1</sup>	3.0×10 <sup>-6</sup>	SO <sub>3</sub> <sup>2-</sup> , Cl <sup>-</sup>	PME	[226]
SO <sub>4</sub> <sup>2-</sup> -10	1,3,5-Triphenylpyrylium perchlorate	-29.7	6.3×10 <sup>-6</sup> -10 <sup>-1</sup>	4.0×10 <sup>-6</sup>	ClO <sub>4</sub> <sup>-</sup> , F <sup>-</sup> , HPO <sub>4</sub> <sup>2-</sup>	PME	[227]
SO <sub>4</sub> <sup>2-</sup> -11	2,6-Diphenyl 4-(4-methoxy-phenyl) pyrylium perchlorate	-29.7	8.0×10 <sup>-7</sup> -10 <sup>-1</sup>	4.0×10 <sup>-7</sup>	-	PME	[228]
SO <sub>4</sub> <sup>2-</sup> -12	N,N'-Bis(2-amino-1-oxo-phenenyl)phenylenediamine copper(II)	-29.5	10 <sup>-7</sup> -10 <sup>-1</sup>	1.0×10 <sup>-8</sup>	CH <sub>3</sub> COO <sup>-</sup> , S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> , SCN <sup>-</sup>	PME	[229]
ClO <sub>4</sub> <sup>-</sup> -1	Ni(II)-hexaazacyclotetradecane	N	5.0×10 <sup>-7</sup> -10 <sup>-1</sup>	2.0×10 <sup>-7</sup>	MnO <sub>4</sub> <sup>-</sup> , SCN <sup>-</sup>	PME	[230]
ClO <sub>4</sub> <sup>-</sup> -2	Phosphorus(V)-tetraphenylporphyrin	-57.8 -53.6	8.0×10 <sup>-6</sup> -1.6×10 <sup>-1</sup> 10 <sup>-6</sup> -3.0×10 <sup>-2</sup>	5.0×10 <sup>-6</sup> 7.0×10 <sup>-7</sup>	I <sup>-</sup> , SCN <sup>-</sup> , CH <sub>3</sub> COO <sup>-</sup>	PME CGE	[231]

**Table 2.** Continued

$\text{ClO}_4^-$ -3	Cobaloxime	-56.8	$10^{-6}$ - $10^{-1}$	$8.3 \times 10^{-7}$	$\text{HPO}_4^{2-}$ , $\text{SO}_4^{2-}$ , $\text{SCN}^-$	PME	[232]
$\text{ClO}_4^-$ -4	1,3,5,8,10,13-Hexaaazacyclotetradecane and 1,8-tert-butyl-1,3,5,8,10,13-hexaaazacyclotetradecane	-59.1 -59.5	$9.0 \times 10^{-7}$ - $10^{-1}$ $5.0 \times 10^{-7}$ - $10^{-1}$	$5.0 \times 10^{-6}$ $7.0 \times 10^{-7}$	$\text{SCN}^-$ , $\text{MnO}_4^-$ , $\text{IO}_4^-$	PME	[233]
$\text{ClO}_4^-$ -5	Two nickel-hexaaazamacrocycles	-60.6	$10^{-6}$ -1	$8.0 \times 10^{-7}$	$\text{F}^-$ , $\text{Cl}^-$ , $\text{NO}_2^-$	PME	[234]
$\text{Cl}^-$	Ruthenium(III) Schiff's base	-29.5	$3.0 \times 10^{-5}$ - $10^{-1}$	$2.0 \times 10^{-6}$	-	PME	[235]
$\text{Br}^-$ -1	14-Phenyldibenzo[a]xanthenium bromide	-61.1	$3.2 \times 10^{-5}$ - $10^{-1}$	$2.0 \times 10^{-5}$	$\text{NO}_3^-$ , $\text{Cl}^-$ , $\text{I}^-$	PME	[236]
$\text{Br}^-$ -2	Bis(4-hydroxyphenyl)-1,4-diaza-1,3-butadiene-Hg(II)	-59.1	$10^{-5}$ - $10^{-1}$	$5.0 \times 10^{-6}$	-	PME	[237]
$\text{Br}^-$ -3	Iron(III)-salen	-59.0	$7.0 \times 10^{-6}$ - $10^{-1}$	$6.0 \times 10^{-6}$	$\text{SCN}^-$ , $\text{I}^-$ , $\text{Cl}^-$	PME	[238]
$\text{I}^-$ -1	Mn(II)-salen	-59.0	$3.4 \times 10^{-5}$ - $10^{-1}$	$1.0 \times 10^{-5}$	$\text{CN}^-$	PME	[239]
$\text{I}^-$ -2	Fe(III) Schiff base	-71.0	$10^{-6}$ - $5.0 \times 10^{-1}$	$6.5 \times 10^{-7}$	$\text{SCN}^-$ , $\text{F}^-$ , $\text{NO}_2^-$	CPE	[240]
$\text{I}^-$ -3	Copper phthalocyanine	57.1	$5.0 \times 10^{-6}$ - $10^{-1}$	$1.0 \times 10^{-6}$	$\text{SCN}^-$ , $\text{ClO}_4^-$	CGE	[241]
$\text{I}^-$ -4	Thiopyrilium ion derivative	-60.2	$8.0 \times 10^{-7}$ - $10^{-1}$	$2.0 \times 10^{-7}$	$\text{SCN}^-$ , $\text{CN}^-$	PME	[242]
$\text{I}^-$ -5	Cerium salen-based	-57.5	$8.0 \times 10^{-6}$ - $5.0 \times 10^{-2}$	$6.0 \times 10^{-6}$	$\text{SCN}^-$	PME	[243]
$\text{I}^-$ -6	Bis(2-mercaptopbenzothiazolato) mercury(II)/bis(4-chlorothiophenolato) mercury(II)	-57.6 -58.4	$10^{-6}$ - $10^{-1}$	$6.0 \times 10^{-7}$ $4.0 \times 10^{-7}$	$\text{SCN}^-$ , $\text{Br}^-$ , $\text{ClO}_4^-$	PME	[244]
$\text{I}^-$ -7	Titanium acetylacetone-based	-59.1	$5.0 \times 10^{-6}$ - $10^{-1}$	$3.0 \times 10^{-6}$	$\text{SCN}^-$ , $\text{Cl}^-$	PME	[245]
$\text{I}^-$ -8	[Tetrakis(4-N,N-dimethylamino-benzene)porphyrinato]-manganese(III) acetate	-59.4	$7.5 \times 10^{-6}$ - $10^{-2}$	$5.0 \times 10^{-6}$	Salicylate, $\text{SCN}^-$ , $\text{ClO}_4^-$	PME	[246]
$\text{I}^-$ -9	Bis[N-(2-methyl-phenyl)-4-nitro-thiobenzamidato]mercury(II)/bis[N-phenyl -3,5-dinitro-thiobenzamidato]mercury(II)	-59.6 -58.9	$7.0 \times 10^{-7}$ - $10^{-1}$ $10^{-6}$ - $10^{-1}$	$3.0 \times 10^{-7}$ $7.0 \times 10^{-7}$	$\text{SCN}^-$ , $\text{ClO}_4^-$	PME	[247]
$\text{I}^-$ -10	Cobalt salophen	-58.9	$5.0 \times 10^{-7}$ - $10^{-1}$	$3.0 \times 10^{-7}$	-	PME	[248]
$\text{I}_3^-$ -1	2,4,6,8-Tetraphenyl-2,4,6,8-tetraaza-bicyclo[3.3.0]octane	-54.7	$3.5 \times 10^{-6}$ - $5.0 \times 10^{-2}$	$2.0 \times 10^{-6}$	-	PME	[249]
$\text{I}_3^-$ -2	Tetra( <i>p</i> -chlorophenyl)porphyrinato manganese(III) acetate	-59.6	$7.0 \times 10^{-6}$ - $10^{-2}$	$5.0 \times 10^{-6}$	$\text{I}^-$ , $\text{ClO}_4^-$	PME	[250]
$\text{I}_3^-$ -3	Ketoconazole-triiodide ion pair	-59.9	$7.0 \times 10^{-6}$ - $2.0 \times 10^{-3}$	$3.0 \times 10^{-6}$	$\text{SCN}^-$ , $\text{IO}_3^-$ , $\text{NO}_2^-$	PME	[251]
$\text{I}_3^-$ -4	Charge-transfer complexes and amino crown ether	-59.0	$10^{-5}$ - $10^{-1}$	$1.0 \times 10^{-6}$	-	PME	[252]

**Table 2.** Continued

$I_3^-$ -5	Two complexes of Schiff base 2,2'-[4,4'-diphenylmethane bis(nitromethylidyne)] bisphenol	-60.0	$8.0 \times 10^{-6}$ - $6.0 \times 10^{-1}$ $10^{-5}$ - $5.0 \times 10^{-1}$	$4.0 \times 10^{-6}$ $6.0 \times 10^{-6}$	SCN <sup>-</sup> , Salicylate	PME	[253]
$I_3^-$ -6	Iodine charge-transfer complex with bis(2-hydroxyaceto-phenone) butane-2,3-dihydrazone	-59.0	$5.0 \times 10^{-7}$ - $10^{-2}$	$3.0 \times 10^{-7}$	-	PME	[254]
$I_3^-$ -7	7,16-Dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane	-59.3	$10^{-5}$ - $10^{-1}$	$6.3 \times 10^{-6}$	-	PME	[255]
$I_3^-$ -8	Mercury-salen	-59.0	$5.0 \times 10^{-5}$ - $10^{-2}$	$2.0 \times 10^{-5}$	-	PME	[256]
$I_3^-$ -9	Copper(II)-Schiff base	-57.0	$10^{-5}$ - $10^{-1}$	$4.8 \times 10^{-6}$	I <sup>-</sup>	CGE	[257]
$I_3^-$ -10	Charge-transfer complex of bis(2,4-dimethoxybenzaldehyde) butane-2,3-dihydrazone with iodine	60.6	$10^{-7}$ - $10^{-2}$	$6.3 \times 10^{-8}$	-	PME	[258]
$I_3^-$ -11	2-((2-((E)-1-(2-Hydroxyphenyl)methylidine) amino) phenyl imino) methyl phenol	-59.0	$5.0 \times 10^{-8}$ - $10^{-2}$	$3.0 \times 10^{-8}$	-	PME	[259]
$I_3^-$ -12	N,N'-1,2-Propylene-bis-(5-methyl salicylidene iminato) copper	-61.4	$4.0 \times 10^{-5}$ - $7.0 \times 10^{-1}$	$1.0 \times 10^{-5}$	I <sup>-</sup> , SCN <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup>	PME	[260]
$I_3^-$ -13	Bis(2-hydroxybenzophenone) butane-2,3-dihydrazone	-59.3	$10^{-7}$ - $10^{-1}$	$7.0 \times 10^{-8}$	-	PME	[261]
CrO <sub>4</sub> <sup>2-</sup> -1	Bis(acetylacetonato)copper(II)	-29.4 -29.2	$5.0 \times 10^{-6}$ - $10^{-1}$	$1.0 \times 10^{-6}$	I <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup>	CWE	[262]
CrO <sub>4</sub> <sup>2-</sup> -2	Bis(acetylacetonato) cadmium(II)	-28.8	$2.5 \times 10^{-6}$ - $10^{-1}$	$1.0 \times 10^{-6}$	I <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup>	CWE	[263]
MoO <sub>4</sub> <sup>2-</sup>	Cerium phosphate	-29.0	$1.98 \times 10^{-5}$ - $10^{-1}$	$1.0 \times 10^{-5}$	SCN <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup>	PME	[264]

summarized information on different anionic sensors reported over the last decade. Normally the detection limits of these sensors have been in the range of  $10^{-7}$ - $10^{-6}$  M. The lowest detection limit reported up to now is about  $1.0 \times 10^{-8}$  M [229].

## SELECTIVE ELECTRODES FOR DRUGS AND ORGANIC SPECIES

There have been plenty of PMEs, CGEs, and CWEs for organic species and drugs which have been summarized in Table 3.

Histamine [265], histidine [266], imidazole [267,268], ketamine [269], ascorbic acid [270], oxalate [271], triamterene [272], naphazoline [273], valproate [274], cystein [275],

theophiline [276], sulfosalicylic acid [277], thiosalicylic acid [278], salicylate [279,280], ketoconazole [281], clotrimazole [282], cimetidine [283], diclofenac [284], atenolol [285], picrate [286], linear alkylbenzene sulfonate [287,288], sodium dodecylsulfate [289-291], dodecylbenzene sulfonate [292] are species the sensors of which have been introduced by Iranian researchers.

Almost all of the developed sensors have proven to show Nernstian responses and relatively low detection limits, and good selectivity behaviors. As it is seen from Table 3, these sensors were based on ionophores like different complexes of iron(III) [265], iron(II) [270], copper(II) [271], zirconyl(IV) [277], nickel(II) [279], tin(IV) [280], lead(II) [275], aluminum(III) [278] and manganese(III) [265], 2,4,6-

**Table 3.** Organic Molecule and Drug Sensors Published by the Iranian Researchers in the Past Decade

Drug	Ionophore	Slope	LR	DL	$\log K_{Sel} > -2$	TS	Ref.
Histamine	Iron(III) and manganese(III) tetraphenyl-porphyrins	56.0	$10^{-6}$ - $10^{-1}$	$5.0 \times 10^{-7}$	$\text{N}_3^-$ , $\text{SCN}^-$ , Imidazole	PME	[265]
Histidine	Chloro(5,10,15,20-tetraphenylporphyrinato) manganese(III)	-55.4	$10^{-5}$ - $10^{-1}$	$5.0 \times 10^{-6}$	L-Histidine	PME	[266]
Imidazole-1	2,4,6-Triphenyl thiopyrilium perchlorate	33.5	$10^{-5}$ - $10^{-1}$	$3.0 \times 10^{-6}$	Histamine, L-Histidin	PME	[267]
Imidazole-2	4-Methyl-2,6-diphenylthio-pyrylium	36.2	$10^{-5}$ - $10^{-1}$	$2.0 \times 10^{-6}$	L-Histidine, $\text{SCN}^-$	PME	[268]
Ketamine	Ion-exchanger sites	59.0	$10^{-5}$ - $10^{-1}$	$5.0 \times 10^{-6}$	Propranolol, Naphazoline, Atropine	PME	[269]
Ascorbic acid	Iron(II) phthalocyanine	58.0	$10^{-6}$ - $10^{-2}$	$5.0 \times 10^{-7}$	-	CPE	[270]
Oxalate	2,2'-[1,4-Butandiyle bis(nitrilopropylidine)]bis-1-naphtholato copper(II)	-29.2	$5.0 \times 10^{-8}$ - $10^{-1}$	$5.0 \times 10^{-8}$	$\text{ClO}_4^-$ , $\text{CH}_3\text{COO}^-$ , $\text{PO}_4^{3-}$	PME	[271]
Triamterene	Tetraphenylborate ion	57.1	$10^{-6}$ - $3.5 \times 10^{-2}$	$5.8 \times 10^{-7}$	Chlordiazepoxide, Primidone, Hydrochlorothiazide	CWE	[272]
Naphazoline	Tetraphenylborate	58.4 57.0	$10^{-5}$ - $5.0 \times 10^{-2}$ / $5.0 \times 10^{-6}$ - $5.0 \times 10^{-2}$	$5.0 \times 10^{-6}$ $4.0 \times 10^{-6}$	Phenylephrine, Betaxolol	PME/ CGE	[273]
Valproate	Conducting polypyrrole films	35.8-47.7	$4.0 \times 10^{-5}$ - $4.0 \times 10^{-2}$	$1.0 \times 10^{-5}$	$\text{PhCOO}^-$ , $\text{CH}_3\text{COO}^-$	SSE	[274]
Cystein	Lead phthalocyanine	N	$10^{-6}$ - $5.0 \times 10^{-2}$	$1.0 \times 10^{-6}$	-	CGE	[275]
Theophiline	2,6-Bis(phenyl)-4(phenyl)-3H-thiopyran	54.5	$10^{-6}$ - $10^{-2}$	$5.5 \times 10^{-7}$	Caffeine, Imidazole, Histidine	PME	[276]
Sulfo-salicylic acid	Zirconyl(IV) phthalocyanine	-29.3	$10^{-6}$ - $10^{-1}$	$8.9 \times 10^{-7}$	$\text{ClO}_4^-$ , $\text{SCN}^-$ , Salicylate	PME	[277]
Thio-salicylic acid	Phthalocyanine complexes of aluminum, nickel and copper	-49.9 -59.5 -60.2	$10^{-5}$ - $10^{-2}$ $10^{-5}$ - $10^{-2}$ $10^{-6}$ - $10^{-2}$	$3.5 \times 10^{-6}$ $1.0 \times 10^{-6}$ $1.0 \times 10^{-6}$	$\text{SCN}^-$ , $\text{ClO}_4^-$ , Salicylate	PME	[278]
Salicylate-1	Bis(trans-cinnamaldehyde) ethylenediamine dibromonickel(II)	59.2	$10^{-5}$ - $10^{-1}$ $10^{-6}$ - $10^{-2}$	$5.0 \times 10^{-6}$ $7.0 \times 10^{-7}$	$\text{ClO}_4^-$ , $\text{SCN}^-$	PME/ CGE	[279]

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**Table 3.** Continued

Salicylate-2	Original tin(IV) complex	58.5	$10^{-6}$ - $10^{-1}$	$8.0 \times 10^{-7}$	SCN <sup>-</sup>	PME	[280]
Ketoconazole	Ketoconazole-tetraphenylborate ion pair	72.0	$7.1 \times 10^{-6}$ - $6.3 \times 10^{-3}$	$5.0 \times 10^{-6}$	-	PME	[281]
Clotrimazole	Phosphomolybdate	59.0	$1.38 \times 10^{-5}$ - $10^{-3}$	$1.0 \times 10^{-5}$	NH <sub>4</sub> <sup>+</sup> , Glycine	PME	[282]
Cimetidine	Phosphohotungstate	58.0	$10^{-5}$ - $10^{-2}$	$5.0 \times 10^{-6}$	K, Na, NH <sub>4</sub>	PME	[283]
Diclofenac	Hexadecylpyridinium bromide	-59.0	$10^{-5}$ - $10^{-2}$	$4.0 \times 10^{-6}$	Na, NO <sub>3</sub> <sup>-</sup>	PME	[284]
Atenolol	Tetrakis( <i>p</i> -chlorophenyl) borate	56.5	$3.0 \times 10^{-5}$ - $8.0 \times 10^{-2}$	$1.0 \times 10^{-5}$	K, Na, Urea	PME	[285]
Picrate	CuI <sup>+</sup> Hg <sup>2+</sup> (Pic) <sup>(2)</sup>	56.8	$2.5 \times 10^{-5}$ - $10^{-2}$	$1.3 \times 10^{-5}$	Cl <sup>-</sup> , Salicylate, Benzoate	CGE	[286]
Linear alkybenzene-sulfonate-1	Polypyrrole	57.2	$3.0 \times 10^{-5}$ - $3.0 \times 10^{-3}$	$2.0 \times 10^{-5}$	Tetradecylsulfate, dodecylsulfate	PME	[287]
Linear alkybenzene-sulfonate-2	Polypyrrole and hyamine	59.7	$8.5 \times 10^{-6}$ - $1.3 \times 10^{-3}$	$5.6 \times 10^{-6}$	Tetradecylsulfate,	CWE	[288]
		56.8	$/5.0 \times 10^{-6}$ - $1.1 \times 10^{-3}$	$2.5 \times 10^{-6}$	dodecylsulfate		
Sodium dodecyl sulfate-1	Polyaniline-dodecyle sulfite	59.0	$10^{-9}$ - $3.0 \times 10^{-6}$	$1.0 \times 10^{-9}$	Dodecyl benzene sulfate	Pt	[289]
Sodium dodecyl sulfate-2	Polypyrrole	57.5	$10^{-5}$ - $7.0 \times 10^{-3}$	$5.0 \times 10^{-6}$	Tetradecylsulfonate, dodecylbenzenesulfonate	PME	[290]
Sodium dodecyl sulfate-3	Cetylpyridinium cation	61.0	$10^{-6}$ - $8.3 \times 10^{-3}$	$6.3 \times 10^{-7}$	Dodecylbenzenesulfonate	PME	[291]
Dodecyl benzene-sulfonate	Polyaniline	-59.1	$5.0 \times 10^{-6}$ - $4.1 \times 10^{-3}$	$1.0 \times 10^{-6}$	Paratoluene sulfonate	Pt	[292]

triphenylthiopyrilium perchlorate [267], 4-methyl-2,6-diphenylthiopyrilium [268], ion-exchanger sites [269], tetraphenylborate ion [272], tetraphenylborate [273], conducting polypyrrole films [274], 2,6-bis(phenyl)-4(phenyl)3H-thiopyran [276], phthalocyanine [278], ketoconazole-tetraphenyl borate ion pair [281], phosphomolybdate [282], phospho tungstate [283], hexadecylpyridinium bromide [284], tetrakis(*p*-chlorophenyl) borate [285], polypyrrole

[287,290], and hyamine [288], polyaniline-dodecylsulfate [289], cetylpyridinium cation [291], polyaniline [292], which have different natures and hence different selection mechanisms.

## CONCLUSIONS

In the past decade, Iranian researchers have had an

exceptional impact in the development of the field of ion sensors in the world, both in quantity and quality. Especially, the contribution of Iranian researchers on the design of ion selective electrodes for lanthanide and actinide ions has been substantial.

Statistically speaking, the sensors designed and reported by Iranian scientists reach to more than 12% of the total number of sensors reported globally. This shows the importance of the Iranian scientists on this vital field of research and the prominent influence of these studies on the global trend of developing chemical sensors.

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