HIGHLY SELECTIVE AND SENSITIVE DETERMINATION OF Hg(II) IONS USING ION SELECTIVE ELECTRODES (ISE) COATED WITH THE BEC4ND1 IONOPHORE AS MEMBRANES

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ABSTRACT

Research on the highly selective and sensitive determination of Hg(II) ions using ion-selective electrodes (ISE) coated with the BEC4ND1 Ionophore as a membrane has been successfully carried out. ISE was designed using the membrane composition of the [(BEC4ND1 ionophore: PTCPB: DOS: PVC) (3: 2 : 60: 35 % w/w)]. The ESI-BEC4ND1 Ionophore has good characteristics. It shows a sensitivity value of 29.933 mV/decade in the Hg(II) ion concentration range of 10^{-9} - 10^{-1} M with a limit of detection (LoD) of 10^{-7} M. The response time is 4 - 8 minutes, with a relative standard deviation (RSD) of 0.548. The ESI-BEC4ND1 Ionophore also shows the average value of selectivity coefficient (K_{ij}) < 1. The presence of Zn(II), Cd(II), and Pb(II) ions as interfering ions in the analyte solution did not affect the performance of the ESI-BEC4ND1 ionophores in detecting Hg(II) ions. The ESI-BEC4ND1 ionophores show good selectivity, sensitivity, stability, and reproducibility, so the ESI-BEC4ND1 ionophores are promising to be used as Hg(II) ion detectors in the environment.

Keywords: *BEC4ND1 ionophore, calyx [4]arene, ISE-Hg(II), membrane, selective.*

INTRODUCTION

The Hg(II) ion is used as a solvent in the processing industry of gold (Au) metal because the Hg(II) ion can dissolve gold metal, forming amalgams. However, the Hg(II) ions are carcinogenic and can damage the kidneys and liver if this metal accumulates in the human body [1-3]. In addition, mercury compounds, such as mercury(II) chloride, are highly toxic because these compounds are soluble in water to form compounds Hg(OH)Cl which can quickly get into the body, causing

death [4]. Therefore, the ion content of Hg(II) in the environment must be monitored regularly.

The Hg (II) ion analysis method that is widely used today is Atomic Absorption Spectrophotometry (AAS) [5] and Cold Vapour Atomic Absorption Spectrophotometry (CVAAS) methods [6-10]. However, the availability of these tools is very limited, and the operational cost is very high. Therefore, it is necessary to develop a method of analysis by considering the cost factor, sensitivity, and good selectivity as ion selective electrodes (ISE).

ISE is a chemical sensor that is widely used for the determination of both cation and anion ions [9]. The ISE method has advantages such as (1) fast and accurate analysis with ISE, (2) ISE can measure the activity of a species directly, (3) ISE has high selectivity, so it does not require separation, (4) comprehensive measurement range, and (5) low cost of analysis [10].

In order to be a selective potentiometric method in the analysis of metal ions, the ionophores compounds can be used as ISE membrane components [11]. Calyx [n]arene is a class of macrocyclic compounds potentially used as ionophores [12-14]. Furthermore, because the structure of the compound resembles a basket, so the compound can be used to interact with neutral ions or molecules [15-16].

One of the ionophores that can be used as membranes at ISE is the BEC4ND1 Ionophore. Because the ionophore BEC4ND1 has 4 [R(OCH$_2$CO$_2$Et)$_4$] groups which can function as ligands (L) that donate free electrons to a metal (M) as the central atom to form a complex compound [MR(OCH$_2$CO$_2$Et)$_4$]. The use of ionophore compounds from calyx

[n]arene derivatives such as *p-tert-*butylcalix[4]arene and *p-tert-*butylcalix[4]-and-[6]arene thioamides have been used as membranes in ISE types coated wire to detect Pb(II), Hg(II), and Au(I) ions [15, 17]. Therefore, it is necessary to study selectivity testing ISE-Hg(II) with ionophore tetra(*p-tert-*butyl)tetra(ethyl ester)-calyx [4]arene (BEC4ND1) against the Zn(II), Cd(II), and Pb(II) ions.

This study offers a new, highly selective, and sensitive way to determine Hg(II) ions using ion selective electrodes (ISE) coated with BEC4ND1 ionophores as membranes. Using BEC4ND1 Ionophores as membranes at ESI showed excellent results for detecting Hg(II) ions in solution. Therefore, this study developed the BEC4ND1 Ionophore as a membrane on ESI to detect Hg(II) ions in solution. The ESI-BEC4ND1 Ionophore is expected to be used as an environmental Hg(II) ion detector.

METHODS

1. Instruments and Materials

The FTIR spectrum was recorded in KBr powder on a Shimadzu® FTIR Prestige-21 spectrometer (Shimadzu Corporation, Kyoto, Japan). The BEC4ND1 Ionophore was synthesized regarding the method reported [13]. The materials used are tetrahydrofuran p.a. (THF) (Merck), aquabidest (Onelab Waterone), HgCl$_2$ p.a. (Merck), Zn(NO$_3$)$_2$ p.a. (Merck), Cd(NO$_3$)$_2$ p.a. (Merck), PbNO$_3$ p.a. (Merck), Ag wire, Cu wire, Pt wire, Sn wire, plasticizer dioctyl sebacate (DOS), poly(vinyl chloride) (PVC) (Fluka), potassium tetrakis(4-chlorophenyl borate) (PTCPB) (Aldrich), parafilm "M" (Pechiney), and a blue tip.

2. Characterization of the ISE-BEC4ND1 Ionophore by FTIR

An FTIR spectrometer characterized the ISE-BEC4ND1 Ionophore synthesized from [13].

3. Design of the ISE-BEC4ND1 Ionophore

The electrode body used a blue tip tube diameter of 2 mm and a length of 7 cm. Platinum (Pt) wire with a diameter of 0.2 mm and a length of 2 cm is connected with copper (Cu) wire contained in the blue tip tube using a soldered tin (Sn) wire. At the top and bottom, electrodes are wrapped with parafilm as retaining Cu and Pt wire. The bottom of the Pt wire is left open, so the membrane can be attached. Furthermore, Pt wire is dipped into a solution of the membrane with the composition [Ionophore: PTCPB : DOS: PVC (3: 2 : 60: 35 % w/w)] [14-15]. The ISE-BEC4ND1 Ionophore has been immersed in a standard solution of Hg(II) of 0.1 M for 24 hours [17].

4. Nernst (Sensitivity) Factor of the ISE-BEC4ND1 Ionophore

Nernst factor value or the ISE-BEC4ND1 ionophore sensitivity is tg α or slope (S) obtained by measuring a series of Hg(II) solutions with concentrations varying from 10^{-9} - 10^{-1} M. The potential measurement starts from the solution with the lowest (10^{-9} M) to the highest (10^{-1} M) concentration. The potential observations were made while stirring with a magnetic stirrer to remove air bubbles on the membrane surface. The measurement results are graphed between the potential value of E (mV) to -log Hg(II). The sensitivity (S) value of the ISE-BEC4ND1 Ionophore is obtained from the value of the regression coefficient b from the linear regression equation $\hat{y} = a + bx$. The value of K is obtained from the value of the regression coefficient a from the linear regression equation = a + bx by extrapolating the linear curve to the y axis [18].

5. Detection Limit of the ISE-BEC4ND1 Ionophore

The detection limit of the ISE-BEC4ND1 Ionophore is the lowest and highest detection limit which still shows a straight line relationship between the potential value of E (mV) and -log [Hg(II)]. The detection limit of the ISE-BEC4ND1 Ionophore was determined by constructing an exponential curve on the Nernstian and non-Nernstian linear regression lines. The intersection points of the exponential curve on the linear regression line indicate the detection limit concentration of the ISE-BEC4ND1 Ionophore [19].

6. The precision of the ISE-BEC4ND1 Ionophore

Precision (accuracy) is the degree of correspondence between repeated measurements of the same number or the level of repetition of the measurement results. Precision is measured as standard deviation (SD). Precision can also be expressed as relative standard deviation (RSD) using Equation 1:

$$RSD = \left(\frac{SD}{\overline{x}}\right) \qquad (1)$$

SD is the standard deviation and ẍ is the average of the measurements [20].

7. Response time of the ISE-BEC4ND1 Ionophore

The response time of the ISE-BEC4ND1 Ionophore is determined based on the length of measurement time required to produce a constant value of potential E (mV). The response time was determined by measuring the various concentrations (10^{-9} - 10^{-1} M) of the standard Hg(II) solution.

8. Selectivity of the ISE-BEC4ND1 Ionophore

The selectivity coefficient of the ISE-BEC4ND1 Ionophore was determined by matched potential method (MPM). For the first

time, a standard electrode potential solution of Hg(II) (major ion) at a concentration of 10^{-9} - 10^{-1} M was measured by the ISE-BEC4ND1 Ionophore in the absence of an interfering ion. Furthermore, electrode potential E (mV) of the solution is measured at each addition concentration of a standard solution of Zn(II), Cd(II), and Pb(II) (interfering ions) in various concentrations of the standard solution of Hg(II) (major ion). The influence of the presence of interfering ions in solution is determined by calculating the coefficient of selectivity. The coefficient of selectivity (K_{ij}) is calculated by Equation 2 [21-22].
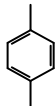
$$K_{ij}^{pot} = \frac{x}{10^{-2}} \qquad (2)$$

The value of x is obtained from the equation of the main ion regression line [23].

RESULTS AND DISCUSSION

1. Characterization of the BEC4ND1 Ionophore by FTIR

Table 1 shows the results of interpreting the FTIR spectrum data of the BEC4ND1 Ionophore.

Table 1. The results of the interpretation of the FTIR spectrum data of the BEC4ND1 Ionophore

No	Frequency (cm^{-1}) and Intensities	Frequency Ranges (cm^{-1}) and Intensities*	Group or Class	Remarks
1	1743.65 (m)	1765 - 1720	Esters	C=O stretch
2	671.23 (w)	675 - 575	RCOOR'	O-C-O bend
5	1244.09 (s)	1280 - 1220 (s)	Ethers ROR'	C-O-C stretch in alkyl aryl ethers
6	1066.64 (m)	1075 - 1020 (s)		R-C-O stretch in alkyl aryl ethers
7	1604.77 (s)	1630 - 1430 (v)	Aromatic ArH	C=C aromatic ring stretching
8	1201.65 (vs)	1300 - 1000 (s)		C-O aromatic ring stretching
9	877.61 (w)	900 - 650 (s)		Out-of-plane C-H deformation
10	846.75 (s)			1,4-disubstituted
11	2958.8 (w)	2970 - 2850 (s)	Aliphatic RH	C-H stretch from saturated $(CH_3)_3C-$
12	2924.09 (w)			
13	2854.65 (w)			
14	1435.04 (s)	1450 - 1375 (s)	*t*-Butyl $(CH_3)_3C-$	C-H stretch from CH_3-
15	1485.19 (w)	1485 - 1450 (m)	Metilen $-CH_2-$	C-H stretch from $-CH_2-$

∘Notes: vs = *very strong*; v = *variable*; s = *strong*; m = *medium*; w = *weak*.

*Sources: [24, 27-28]

The FTIR spectrum analysis of the BEC4ND1 Ionophore (Table 1) showed the presence of ester, ether, aromatic, and aliphatic functional groups. The absorption bands at 1743.65 and 671.23 cm^{-1} were from the C=O ester stretch and the O-C-O ester bend,

respectively. According to [24], the absorption band in the range of 675 - 575 cm^{-1} is typical for bending O-C-O esters. The ether functional group showed two absorption bands, a strong absorption band at 1244.09 cm^{-1}, which came from the C-O-C stretch in alkyl aryl ethers and

a moderate absorption band at 1066.64 cm^{-1}, which came from the R-C-O stretch in alkyl aryl ethers. The strong absorption bands at 1604.77 and 1201.65 cm^{-1} were from the C=C stretch of the aromatic ring and the C-O stretch of the aromatic ring, respectively. Meanwhile, the strong absorption band at 877.61 and 846.75 cm^{-1} is derived from the out-of-plane C-H deformation of the 1,4-disubstituted aromatic ring. The three absorption bands that appear at 2958.8, 2924.09, and 2854.65 cm^{-1} are from the saturated aliphatic C-H stretch of the methyl (-CH$_3$) group. Meanwhile, the other two absorption bands that appear at 1435.04 and 1485.19 cm^{-1} are from the C-H stretch of the *t*-butyl [(CH$_3$)$_3$C-] group and the C-H stretch of the methylene (-CH$_2$-) group. All absorption regions found in the FTIR spectrum of the BEC4ND1 ionophore sample are by the results of studies reported by previous researchers [13, 25-26].

2. Nernst (Sensitivity) Factor of the ISE-BEC4ND1 Ionophore

The results of measuring the potential value of Hg(II) ion at a concentration of 10^{-9} - 10^{-1} M using the ISE-BEC4ND1 Ionophore are presented in Table 2.

Table 2. The results of measuring the potential value of Hg(II) ion at a concentration of 10^{-9} - 10^{-1} M

No	The concentration of Hg(II) [M]	-log [Hg(II)]	Potential Value E (mV)
1	10^{-9}	9	258.4
2	10^{-8}	8	285.3
3	10^{-7}	7	313.8
4	10^{-6}	6	340.3
5	10^{-5}	5	373.1
6	10^{-4}	4	398.7
7	10^{-3}	3	438.5
8	10^{-2}	2	463.5
9	10^{-1}	1	496.8
Nernst Factor (S)		29.933 mV/dekade	
E^o (K)		523.93	
R^2		0.9983	

Based on the data in Table 2, Equation 3 is obtained for potential linear regression and Equation 4 for linear regression y over x as follows:

$$E = (523.93 \pm 1.7) + (29.933 \pm 0.1) \log [Hg^{2+}] \quad (3)$$
$$\hat{Y} = (523.93 \pm 1,7) + (29.933 \pm 0,1) x \quad (4)$$

Equation 3 shows that the potential value in the linear region decreases as the concentration of Hg(II) metal decreases. Equation 4 shows the coefficient of linear regression direction [(b) $\approx$ (29.933 $\pm$ 0.1)]. If x {(-log [Hg(II)]} increases by one unit, then the average y (potential value) decreases by (29.933 $\pm$ 0.1) mV/decade.

The Nernst (sensitivity) factor is the change in analyte concentration and the slope value of the curve obtained at a certain concentration [18]. A large sensitivity value gives a small change in the concentration of the analyte and gives a significant response. The sensitivity characteristics can be determined from the linearity curve regression equation. Sensitivity is the slope (b) value of the linear regression equation $\hat{y} = a + bx$. The data in Table 2 shows that the sensitivity value of the ISE-BEC4ND1 Ionophore in detecting Hg(II) ions is 29.933 mV/decade. These results indicate that the sensitivity of the ISE-BEC4ND1 Ionophore is very high because the Nernst factor value is the same as the theoretical value (29.6 $\pm$ 1.5) mV/decade for divalent ions. These results indicate that the concentration of the BEC4ND1 Ionophore used can increase membrane permeability. Permeability is a property of membrane performance that shows membrane productivity [29].

3. Detection Limit of the ISE-BEC4ND1 Ionophore

Figure 1 shows a linear regression graph of the relationship of -log [Hg(II)] with the potential value of the ISE-BEC4ND1 Ionophore.
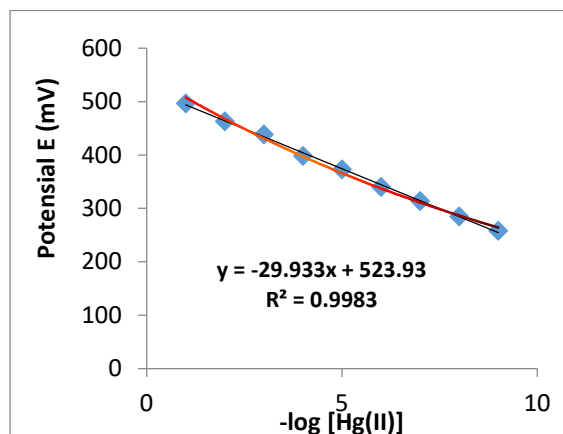

The graph shows: y = -29.933x + 523.93, R² = 0.9983

Figure 1.   Linear regression graph of the relationship of -log [Hg(II)] with the potential value of the ISE-BEC4ND1 Ionophore

The limit of detection (LoD) is the lowest concentration of analyte in the sample that can be detected or measured consistently by the electrode [30]. The LoD of the ISE-BEC4ND1 Ionophore was determined by constructing an exponential curve on the Nernstian and non-Nernstian linear regression lines. Figure 1 shows that there are two intersection points of the exponential curve (red line) on the linear regression line (blue line) at 10^{-7} and 10^{-2} M of Hg(II) ion concentrations. Therefore, it can be indicated that the working concentration of ISE-BEC4ND1 Ionophore ranges from 10^{-7}M (lowest) to 10^{-2}M (highest). Thus, the 10^{-7} - 10^{-2} M concentration range is considered the best for measuring Hg(II) metal ions using the ISE-BEC4ND1 Ionophore. Because, in the concentration range of 10^{-7} - 10^{-2} M, the ISE-BEC4ND1 Ionophore can consistently detect or measure the concentration of Hg(II) ions in the sample. The results of this study are also to the results of other researchers who showed that the concentration range of $10^{-7} – 10^{-2}$ M is the best concentration range for the measurement of heavy metal ions in a sample solution [13, 17, 23, 31-33, 37].

Figure 1 also shows that the lowest concentration limit (LoD) of the ISE-BEC4ND1 Ionophore in detecting Hg(II) ions is 10^{-7} M. These results indicate that the designed ISE-BEC4ND1 ionophore has a wide linear range and lower detection limit. The ISE-BEC4ND1 Ionophore is designed with platinum wire 0.2 mm in diameter and 2 cm long as the working electrode, the membrane composition [BEC4ND1 ionophore : PTCPB : DOS: PVC (3 : 2: 60: 35% w/w)], and the properties of the BEC4ND1 ionophores as membrane component materials have a significant effect on the value of the Nernst factor. According to the statement [31], the value of the Nernst factor is influenced by the electrode geometry, the diameter of the wire in contact with the membrane, the composition of the membrane, and the properties of the components of the membrane material. At the same time, the thickness of the membrane has no significant effect.

4. The precision of the ISE-BEC4ND1 Ionophore

Precision is a measure of how well test results can be reproduced. Precision is measured as standard deviation (SD) or relative standard deviation (RSD). RSD can be calculated from the data in Table 2 using Equation 1 as follows:

$$RSD = \left(\frac{2.74}{5}\right) = 0.548……..(5)$$

The result of the above calculation shows that the RSD value of the ISE-BEC4ND1 Ionophore is 0.548. The RSD value of 0.548 is less than 2. The smaller the RSD value, the higher the measurement precision of an electrode [32]. The ISE-BEC4ND1 Ionophore has a very high precision or repeatability of the measurement results for the very high Hg(II) ion potential value.

5. Response time of the ISE-BEC4ND1 Ionophore

The response time of the ISE-BEC4ND1 ionophores is determined based on the length of time required to produce a constant potential value. The response time was determined by measuring the standard Hg(II) solution at concentrations between 10^{-9} - 10^{-1} M.

The response time is required for an electrode to reach a stable and constant potential value [18]. For example, the response time of the ISE-BEC4ND1 Ionophore is approximately 4 - 8 minutes. Therefore, the time required for the ISE-BEC4ND1 Ionophore to produce a constant value of potential is about 4 - 8 minutes. This response time indicates the electron transfer rate from the BEC4ND1 ionophore membrane on the electrode surface to Hg(II) ions to provide an accurate measurement response. The higher the concentration of Hg(II) ions in the analyte, the faster the $[R(OCH_2CO_2Et)_4]$ groups of the BEC4ND1 Ionophore interact with the Hg(II) ions to form complex compounds of $[HgR(OCH_2CO_2Et)_4(Cl_2)]$. Following the results of other studies, the greater the concentration of metal ions in the analyte solution, the faster the time required to form compounds or complex products. [13, 17, 23, 31-33, 37].

6. Selectivity of the ISE-BEC4ND1 Ionophore

The results of the measurement of the selectivity coefficient (K_{ij}) of the ISE-BEC4ND1 Ionophore on the main ion Hg(II) with a concentration of 10^{-9} - 10^{-1} M against the interfering ions the Zn(II), Cd(II), and Pb(II) are sequentially presented in the Tables 3, 4, and 5.

Table 3. The selectivity coefficient (K_{ij}) of the ISE-BEC4ND1 Ionophore on the interfering Zn(II) ions

-log [Zn(II)]	E (mV)	K_{ij}
9	363,4	$-1,37 \times 10^{-3}$
8	362,7	$-1,23 \times 10^{-4}$
7	362,6	$-1,03 \times 10^{-5}$
6	372,2	$-8,18 \times 10^{-2}$
5	340,3	$-1,17 \times 10^{-2}$
4	298,5	$-1,28 \times 10^{-1}$
3	429,5	$-7,28 \times 10^{-1}$
2	265,3	-13,76
1	415,3	-78,16

Table 4. The selectivity coefficient (K_{ij}) of the ISE-BEC4ND1 Ionophore on the interfering Cd(II) ions

-log [Cd(II)]	E (mV)	K_{ij}
9	364,1	$-1,29 \times 10^{-2}$
8	334,6	$-1,09 \times 10^{-3}$
7	299,1	$-1,29 \times 10^{-4}$
6	449,5	$-1,06 \times 10^{-1}$
5	430,1	$-7,48 \times 10^{-3}$
4	334,7	$-1,09 \times 10^{-1}$
3	430,5	$-7,42 \times 10^{-1}$
2	334,5	-10,99
1	430,3	-75,49

Table 5. The selectivity coefficient (K_{ij}) of the ISE-BEC4ND1 Ionophore on the interfering Pb(II) ions

-log [Pb(II)]	E (mV)	K_{ij}
9	362,2	$-1,32 \times 10^{-2}$
8	353,9	$-3,77 \times 10^{-3}$
7	301,7	$-1,84 \times 10^{-4}$
6	448,5	$-1,08 \times 10^{-1}$
5	429,6	$-7,32 \times 10^{-3}$
4	333,7	$-1,06 \times 10^{-1}$
3	429,5	$-7,28 \times 10^{-1}$
2	353,5	-3,97
1	419,4	-105,89

Tables 3, 4, and 5 show the average values of the selectivity coefficient (K_{ij}) < 1. The presence of the Zn(II), Cd(II), and Pb(II) ions in the solution does not interfere with the performance of the ISE-BEC4ND1 Ionophore. The results above show that the [R(OCH$_2$CO$_2$Et)$_4$] groups of the BEC4ND1 Ionophore are selective for Zn(II), Cd(II), and Pb(II) ions. Selectivity of the BEC4ND1 Ionophore toward the Zn(II), Cd(II), and Pb(II) ions is related to the nature of hard, soft acids bases (HSAB). The stability of complex compounds is based on the suitability of the size of the metal ions with the ionophore ring size [32-33]. The Zn(II) and Pb(II) ions include acids intermediate [35] so that the Zn(II) and Pb(II) ions cannot interact with the O-carbonyl atom and the O-ether atom. Soft bases [34] from the [R(OCH$_2$CO$_2$Et)$_4$] groups of the BEC4ND1 Ionophore to form complex compounds of the [ZnR(OCH$_2$CO$_2$Et)$_4$(NO$_3$)$_2$] and [PbR(OCH$_2$CO$_2$Et)$_4$(NO$_3$)$_2$] [14]. Otherwise, the Cd(II) and Hg(II) ions are acidic and soft [34]. So that the Cd(II) and Hg(II) ions can interact with the O-carbonyl atom and the O-ether atom, which are soft bases [34] from the [R(OCH$_2$CO$_2$Et)$_4$] groups of the BEC4ND1 Ionophore to form complex compounds of the [CdR(OCH$_2$CO$_2$Et)$_4$(NO$_3$)$_2$] and [HgR(OCH$_2$CO$_2$Et)$_4$(Cl$_2$)] were relatively stable [14]. Nevertheless, the complex compounds formed by the Hg(II) ion are more stable than the Cd(II) ion due to differences in both acidic nature, i.e. the Hg(II) ion is more lenient than the Cd(II) ion [34].

Molecular ring size is one factor that determines the selectivity of calyx [n]arene against a metal ion. The results of the study extraction of the Na$^+$ and K$^+$ ions with *p-tert*-butylcalix[n]arenetetraethylester (n = 4, 6, and 8) as extractant showed that the Na$^+$ ion (r = 1.18 Å) extractable effective when the extracted with

compounds of *p-tert*-butylcalix[4]arenetetraethylester, while the K$^+$ ion (r = 1.51 Å) extractable effective when the extracted with compound of *p-tert*-butylcalix[6]arenetetraethylester [35]. This fact shows that the ionic radius of the Zn(II) ion (r = 0.74 Å) and Cd(II) ion (r = 0.97 Å) < radius of the Na$^+$ ion (r = 1.18 Å) [24], so that the size of the Zn(II) and Cd(II) ions does not match the ring size of the BEC4ND1 ionophore. Similarly, the ionic radius of the Pb(II) ion (r = 1.29 Å) > radius of the Na$^+$ ion (r = 1.18 Å) [36], so the size of the Pb(II) ion is also incompatible with the ring size of the BEC4ND1 Ionophore. While the ionic radius of the Hg(II) ion (r = 1.10 Å) $\approx$ radius of the Na$^+$ ion (r = 1.18 Å) [36], the size of the Hg(II) ion is more appropriate to the ring size of the BEC4ND1 Ionophore.

The process of metal ion reaction with the BEC4ND1 Ionophore does not involve the mechanism of ion exchange but through the formation of a neutral complex with the ion pairs of anionic salts [37]. The formation of complex compounds between Hg(II) ions and the BEC4ND1 Ionophore involves chloride ions as complex ion pairs. The reaction for the formation of this complex does not involve proton exchange. However, it only involves metal ions Hg(II) as electron-pair acceptors from the oxygen donor from the [R(OCH$_2$CO$_2$Et)$_4$] groups of the BEC4ND1 Ionophore. When four molecules of the BEC4ND1 Ionophore as ligands donate their lone pairs to the central metal ion Hg(II) to form a coordinating covalent bond, a complex compound of the [HgR(OCH$_2$CO$_2$Et)$_4$(Cl$_2$)] is formed. The approximate structure of the complex compound of the tetra ethyl ester mercury(II) chloride [HgR(OCH$_2$CO$_2$Et)$_4$(Cl$_2$)] is shown in Figure 2.
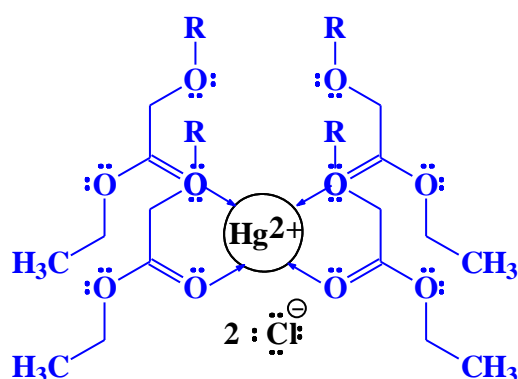
Complex of [HgR(OCH₂CO₂Et)₄(Cl₂)]
(Complex of tetra ethyl ester mercury(II) chloride)

Figure 2.   The approximate structure of the complex compound of the tetra ethyl ester mercury(II) chloride [HgR(OCH₂CO₂Et)₄(Cl₂)]. Writing the structure of the BEC4ND1 Ionophore is simplified with only writing the [R(OCH₂CO₂Et)₄] groups at the bottom of the aromatic ring.

The overall reaction:

$$[Hg(OH_2)_4](Cl_2) \quad + \quad [R(OCH_2CO_2Et)_4] \quad \longrightarrow \quad [HgR(OCH_2CO_2Et)_4](Cl_2)] \quad + \quad 4\ H_2O$$
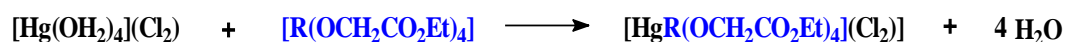
Tetra aquo mercury(II) chloride Tetra ethyl ester   Complex of tetra ethyl ester   Water
   in aqueous solution (BEC4ND1 ionophore groups)   mercury(II) chloride

Mechanism of the reaction:

Tetra aquo mercury(II) chloride and   **Transition State**   Complex of [HgR(OCH₂CO₂Et)₄(Cl₂)]
   BEC4ND1 ionophore groups   (Complex of tetra ethyl ester mercury(II) chloride
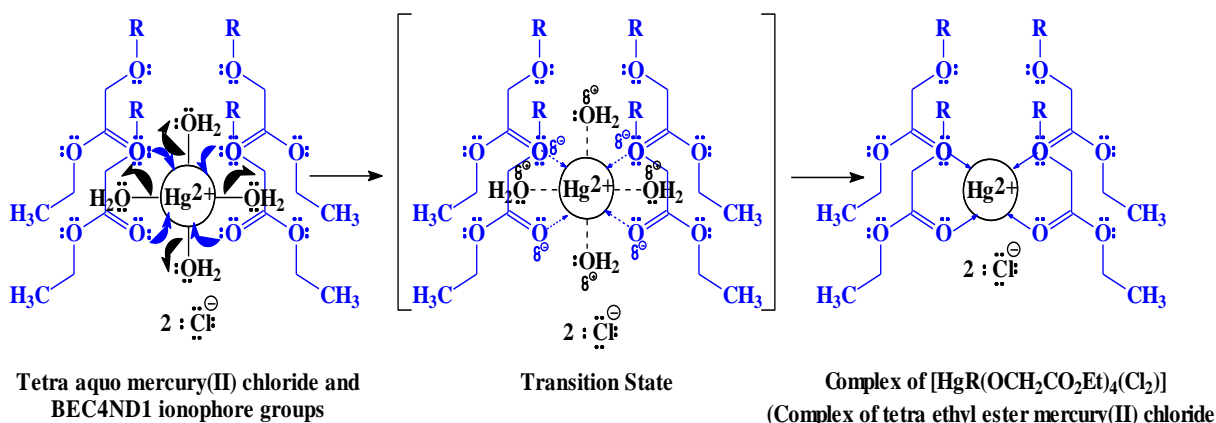
Figure 3.   The approximate S_N2 reaction mechanism for the formation of the complex compound of the [HgR(OCH₂CO₂Et)₄(Cl₂)] between the [R(OCH₂CO₂Et)₄] groups of the BEC4ND1 Ionophore and the Hg(II) ion. Writing the structure of the BEC4ND1 Ionophore is simplified with only writing the [R(OCH₂CO₂Et)₄] groups at the bottom of the aromatic ring.

The approximate reaction mechanism for the formation of the complex compound of the $[HgR(OCH_2CO_2Et)_4(Cl_2)]$ between the $[R(OCH_2CO_2Et)_4]$ groups of the BEC4ND1 Ionophore and the Hg(II) ion is shown in Figure 3. The reaction mechanism for the formation of the complex compound $[HgR(OCH_2CO_2Et)_4(Cl_2)]$ is thought to follow the mechanism of the substitution nucleophilic bimolecular (S_N2) reaction. The mechanism of the S_N2 reaction between the $[R(OCH_2CO_2Et)_4]$ groups of the BEC4ND1 Ionophore (ligand) as a nucleophile ($Nu:^-$) attacks the Hg^{2+} ion (central ion), which binds H_2O as a leaving group (LG) to form a transition state. When H_2O (LG) takes its bonding electron pair with it, the $[R(OCH_2CO_2Et)_4]$ groups of the BEC4ND1 Ionophore ($Nu:^-$) donates its lone pair to the Hg^{2+} ion (central ion) for the formation of the complex compound of the $[HgR(OCH_2CO_2Et)_4(Cl_2)]$ as the product of the S_N2 reaction.

CONCLUSION

The ESI-BEC4ND1 ionophore showed very high sensitivity (S = 29.933 mV/decade), selectivity (Kij < 1), and accuracy (RSD = 0.548) in detecting Hg(II) ions. Therefore, the ESI-BEC4ND1 Ionophore is promising to be used as an environmental Hg(II) ion detector.

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