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Complex equilibrium study of some hydroxy aromatic ligands with beryllium ion

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ABSTRACT

Equilibrium studies of beryllium with 2,3-dihydroxybenzoic acid, 3,4-dihydroxybenzoic acid and gallic acid in an aqueous solution at 310.15 K, an ionic strength of 0.15 mol·dm^{-3} NaCl and pH 2.5 to 11.0 were investigated by the pH-potentiometric method. Stability constants of the complexes were determined by HyperQuad2008 and presented as logβ. Contributing binding sites of these ligands were evaluated by comparing its logβ with some structurally related ligands such as catechol and salicylic acid. Spectrophotometric measurements were done to confirm the formation of the complex species. Geometry optimization and frequency analysis of the complexes were performed by using Gaussian09W program to verify the contributing binding sites. The results indicate that the ability of ligands in preventing the hydrolysis of Be^{2+} follows the order: 3,4-dihydroxybenzoic acid > 2,3-dihydroxybenzoic acid > gallic acid.

1. Introduction

Beryllium is a considerably toxic element which may induce abnormal cell growth in the lung, known as chronic beryllium disease (CBD). Exposure to this metal may cause fatal health effect [1–3]. Moreover, beryllium is known as an amphoteric species which is reactive in both acidic and basic environment, thus greatly increases the possibility of its exposure. Studies about the chemistry of Be^{2+} in an aqueous solution showed that Be^{2+} is able to form various hydroxo species. For example $[Be_2(OH)]^{3+}$ and $Be(OH)_2$ are formed during hydrolysis of beryllium [4,5], while $[Be(OH)_4]^{2-}$ and $[Be_2(OH)_7]^{3-}$ can be found in highly acidic and basic environment, respectively [6]. The addition of organic ligands into beryllium solution may prevent the formation of these hydroxo species, where the active donor atom of the ligand will bind the Be^{2+} ion instead of hydroxo ions [7–12].

Based on Pearson's Hard Soft Acid Base (HSAB) theory, hard acid ion such as Be^{2+} tends to form strong chelate complex with hard base ligand [13]. Thus in this work, hydroxy aromatic ligands 2,3-dihydroxybenzoic acid (DA), 3,4-dihydroxybenzoic acid (PA) and gallic acid (GA) were used as the ligand to form complex with Be^{2+}. These compounds are categorized as hard bases which possess at least three oxygen donor atoms in their carboxyl (−COOH) and hydroxyl (−OH) functional groups. These natural phytochemicals can be found in aquatic ferns, tea leaves, gallnuts, oak barks and many other plants. They are biologically significant for humans due to their antioxidant, antimicrobial and anti-inflammatory properties [14–16].

During complexation, these antioxidants may coordinate with Be^{2+} in several possible binding modes, in particular DA may form complex in salicylate or catecholate manner as depicted in Fig. 1 [17,18]. It was an interesting subject to study the ligand possible binding modes towards metal ion. Therefore to gain an insight into the contributing binding sites of the studied ligands, the complexation properties of catechol (CAT) and salicylic acid (SAL) were also studied. The aim of this work was to determine the complexing ability of DA, PA and GA along with CAT and SAL towards Be^{2+} by the potentiometric method at 310.15 K and an ionic strength of 0.15 mol·dm^{-3} NaCl in an aqueous solution. These complexing ability properties were determined by using HyperQuad2008 program and quantitatively presented as stability constants (logβ), while qualitatively the complex formation was observed by using spectrophotometric measurement. The species distribution diagrams in the pH range of 2.5 to 11.0 obtained from HySS2009 were graphically presented. The complex structures were verified by the density functional theory calculation method using Gaussian09W program.

2. Experimental section

2.1. Materials and solutions

Beryllium sulfate tetrahydrate ($BeSO_4·4H_2O$, 98% purity), 2,3-dihydroxybenzoic acid ($C_7H_6O_4$, 99% purity) and 3,4-dihydroxybenzoic acid ($C_7H_6O_4$, 97% purity) were obtained from Alfa Aesar (Lancashire, UK). Gallic acid ($C_7H_6O_5$, 97.5% purity) was acquired from Sigma Aldrich

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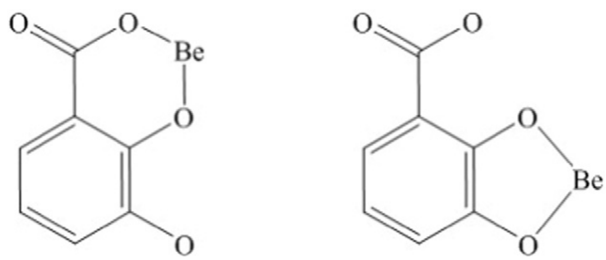

Fig. 1. DA binding mode in salicylate (left) and catecholate (right) manner.

(Steinheim, Germany). Catechol ($C_6H_6O_2$, 99% purity) and hydrochloric acid (HCl, 37.6%) were purchased from Fisher Scientific (Waltham, MA). Salicylic acid ($C_7H_6O_3$, 99% purity) was supplied by Shimakyu (Osaka, Japan), Carbonate-free sodium hydroxide (NaOH, 96% purity) and sodium chloride (NaCl, 99.5% purity) were obtained from Yakuri Pure Chemical (Kyoto, Japan) and Showa (Tokyo, Japan), respectively. All solutions in this study were prepared freshly before use in distilled deionized water (resistance 18.3 MΩ·cm). The beryllium sulfate tetrahydrate solution, NaOH and HCl were standardized before use.

2.2. Potentiometric method

All titrations were carried out in a 150 cm^3 glass vessel which was connected to a thermostated circulating bath to maintain the temperature at 310.15 K. The determination of stability constants of metal-ligand complexes was done by titrating a mixture of solution containing 0.0004–0.001 $mol \cdot dm^{-3}$ of Be^{2+} salt (T_M) + 0.001–0.0012 $mol \cdot dm^{-3}$ of ligand DA/PA/GA/CAT/SAL (T_L), where the T_M to T_L ratios used were

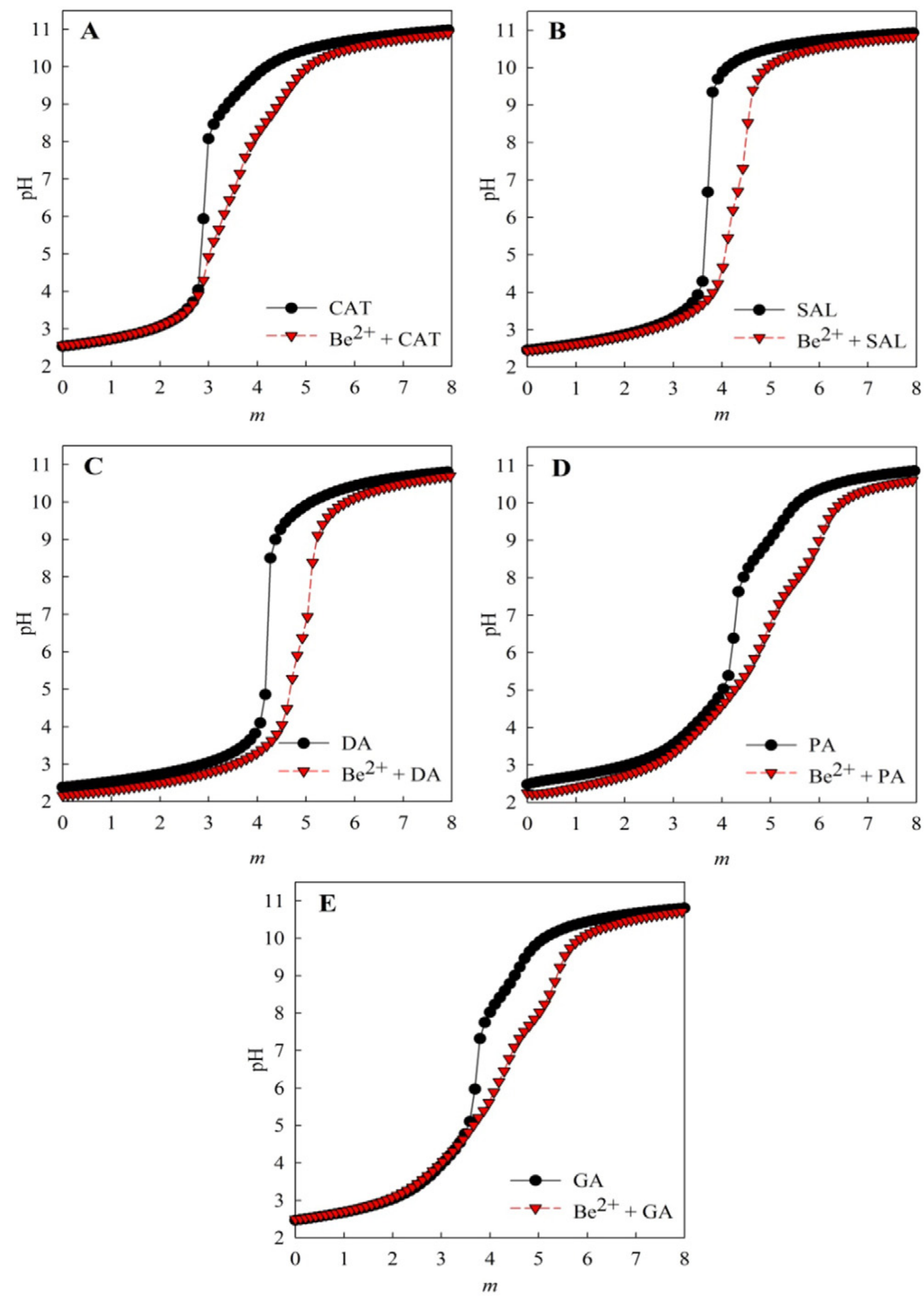

Fig. 2. Titration curve of the Be^{2+}–ligand system with M:L ratio 1:2.5, where *m* is moles of base added per mole of ligand.

Table 1
Stability constant of Be^{2+} complex at T = 310.15 K and I = 0.15 mol·dm^{-3} NaCl.

p	q	r	Species[a]	$\log\beta_{pqr}(u)$[b] CAT	SAL	DA	PA	GA
BeL–core species								
1	1	3	[$BeLH_3$]	–	–	–	–	35.68(6)
1	1	2	[$BeLH_2$]	–	–	25.53(5)	24.31(9)	31.50(5)
1	1	1	[BeLH]	20.12(1)	15.69(10)	20.95(9) 20.24[d]	19.91(3)	22.50(9)
1	1	0	[BeL]	13.54(1) 13.52[c]	12.69(5) 12.69[d]	13.68(6)	13.50(1)	13.81(9)
BeL2–core species								
1	2	2	[BeL_2H_2]	–	32.46(10)	39.35(6) 37.93[c]	38.90(5)	–
1	2	1	[BeL_2H]	30.89(2)	29.12(3)	29.64(3) 29.02[c]	31.22(7)	31.29(8)
1	2	0	[BeL_2]	22.42(2) 23.35[c]	22.56(3) 22.34[c]	18.98(8)	23.14(8)	20.35(8)

[a] Charge of the species is ignored for simplification.
[b] Coefficients *p*, *q*, and *r* in the log β_{pqr} represent the number of Be^{2+} ion, ligand and H^+ proton, respectively. Values in parentheses are the standard deviation of the last decimal place; ±95% confidence interval.
[c] Ref. [23].
[d] Ref. [24].

Table 2
Stepwise formation constants of Be^{2+} complexes.

Ligand	$\log K_{MLH_{(n-1)}}$[a]	$\log K_{ML}$[b]	$\log K_{ML_2}$[c]
CAT	7.12	13.54	8.88
SAL	2.69	12.69	9.87
DA	2.55	13.68	5.30
PA	2.59	13.50	9.64
GA	2.98	13.81	6.54

[a] Values of $\log K_{MLH_{(n-1)}}$ were obtained by the following equation:

$$\text{CAT or SAL}: \log K_{MLH_{(n-1)}} = \log\beta_{111} - pK_{a_2}; n = 2$$
$$\text{DA or PA}: \log K_{MLH_{(n-1)}} = \log\beta_{112} - pK_{a_2} - pK_{a_3}; n = 3$$
$$\text{GA}: \log K_{MLH_{(n-1)}} = \log\beta_{113} - pK_{a_2} - pK_{a_3} - pK_{a_4}; n = 4$$

[b] Values of $\log K_{ML} = \log\beta_{110}$ for all systems.
[c] Values of $\log K_{ML_2} = \log\beta_{120} - \log K_{ML}$ for all systems.

1:1, 1:2, 1:2.5 and 1:3. The ionic strength of each solution was maintained with 0.15 mol·dm^{-3} NaCl and the solutions were initially acidified by adding 0.003 mol·dm^{-3} HCl. The solutions were titrated against standardized carbonate-free NaOH under nitrogen atmosphere.

All titrations were performed using a Metrohm 888 Titrando with 805 dosimat and equipped with a 802 rod stirrer and an Ecotrode Plus pH-glass electrode with pH unit readability up to third digit decimal. Calibration of the electrode was evaluated by means of strong acid-strong base titration using GLEE program. This potentiometer was connected to a personal computer equipped with Tiamo 2.3 titration software to record the titration data. Each set of titration was repeated at least 3 times with repeatability of ±0.02 in pH unit. The data then were used for the determination of stability constants from refinement using HyperQuad2008 program [19]. The stability constants were presented as $\log\beta_{pqr}$ values, which can be expressed as follows:

$$p\mathrm{Be} + q\mathrm{L} + r\mathrm{H} \rightleftharpoons \mathrm{Be}_p\mathrm{L}_q\mathrm{H}_r; \qquad \log\beta_{pqr} = \frac{[\mathrm{Be}_p\mathrm{L}_q\mathrm{H}_r]}{[\mathrm{Be}]^p[\mathrm{L}]^q[\mathrm{H}]^r}$$

where *p*, *q* and *r* are the number of Be^{2+}, ligand and H^+ involved in the species formation, respectively. After the stability constants of various complex species were obtained, species distribution of each system was graphically presented by using the HySS2009 program [20].

2.3. Spectrophotometric measurement

The formation of the complexes was confirmed spectrophotometrically. The measurements were performed by using a double-beam Jasco V-550 spectrophotometer and a standard 10 mm quartz cell. The range of wavelength used in the measurement is 200 to 500 nm. The solutions were prepared (each 50 cm^3 in total) as follow: (a) 0.0004 mol·dm^{-3} ligand solution and (b) 0.0004 mol·dm^{-3} ligand +0.00016 mol·dm^{-3} metal solution.

2.4. Molecular modeling

The complex structures were optimized by the density functional theory (DFT) method with B3LYP exchange-correlation function and 6-311++G(d) basis set. Along with geometry optimization, frequency calculations were also carried out using Gaussian09W program [21]. For simplification purpose, (a) the addition of salt and base in the system was not included in the calculation, (b) the calculations were only intended for the BeL–core species and (c) the complex structures were evaluated from their free energy values.

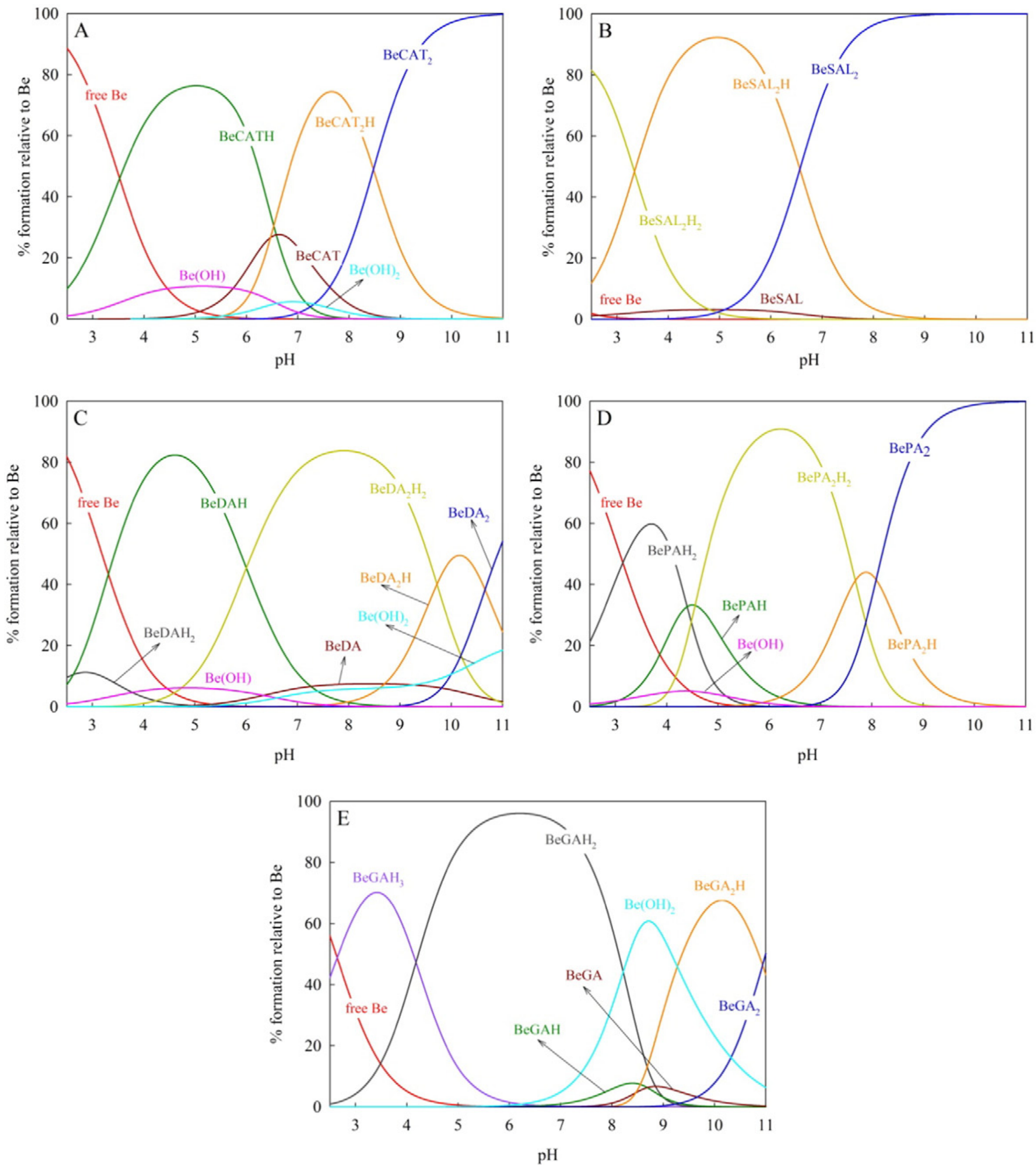

Fig. 3. Species distribution diagram of Be^{2+} with (a) CAT, (b) SAL, (c) DA, (d) PA and (e) GA; metal to ligand molar ratio of 1:2.5.

3. Results and discussion

3.1. Stability constant of beryllium complexes

The ligands used in this work are the hydroxy aromatic ligands (DA, PA, GA, CAT and SAL) which contain both carboxylic (−COOH) and hydroxyl (−OH) donor groups, except for CAT which only has –OH groups. The protonation constants of the ligands were examined and compared with those reported in the literatures [22,23] and the results show good agreement. In the case of protonation constants which have value >11, the values obtained from the literatures [22,23] were inputted into the HyperQuad2008 for the determination of stability constants. The hydrolysis constants of Be^{2+} species such as $Be(OH)^+$, $Be(OH)_2$, $Be_2(OH)^{3+}$ and $Be_3(OH)_3^{3+}$ were also examined and compared with those reported in the literature [5].

The formation of the metal complex indicated by the inflection point which occur at approximately $m = 4$ for all systems as shown in the titration curves in Fig. 2. The species observed in the system of Be^{2+} with hydroxy aromatic ligands were the BeL–core species ($BeLH_3$, $BeLH_2$, BeLH and BeL) and the BeL_2–core species (BeL_2H_2, BeL_2H and BeL_2). The refined stability constants from HyperQuad2008 are presented in Table 1.

The stepwise formation constants of the species were calculated and these values are given in Table 2. Stepwise formation constant (log$K$) corresponds to stepwise addition of one proton/ligand at a time, while stability constant (logβ) corresponds to the addition of protons/ligands

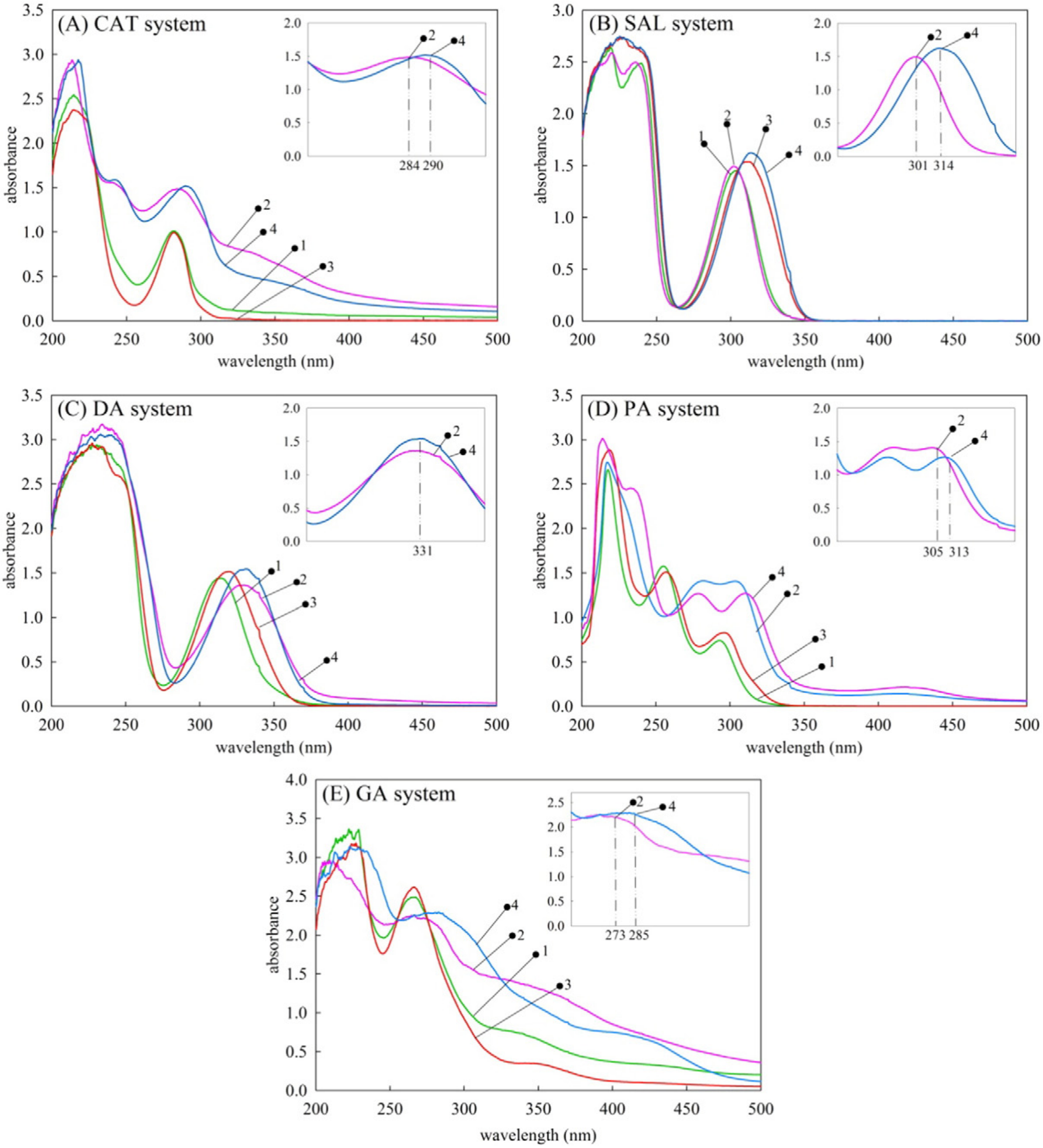

Fig. 4. Spectrum of beryllium–ligand complexes with metal to ligand molar ratio of 1:2.5, where (1) ligand only at pH 7, (2) ligand only at pH 11, (3) Be^{2+} + ligand at pH 7 and (4) Be^{2+} + ligand at pH 11.

all at once or known as overall formation constant. $\log K_{MLH_{(n-1)}}$ represents the stepwise formation constant of the earliest species which is formed from the binding of Be^{2+} via the –COOH group of ligand, following the steps described below:

$$Be^{2+} + LH^- \rightleftharpoons BeLH^+ \quad ; L = \text{CAT or SAL} \tag{1}$$

$$Be^{2+} + LH_2^- \rightleftharpoons BeLH_2^- \quad ; L = \text{DA or PA} \tag{2}$$

$$Be^{2+} + LH_3^- \rightleftharpoons BeLH_3^+ \quad ; L = \text{GA.} \tag{3}$$

These species have similar $\log K_{MLH_{(n-1)}}$ values of 2.69, 2.55, 2.59 and 2.98 for SAL, DA, PA and GA, respectively which indicate that the same contributing donor atom was bound to the metal ion, in this case the –COOH group (except for CAT which has a $\log K_{MLH_{(n-1)}}$ of 7.12 and bound through one –OH group). The species distribution diagrams in Fig. 3 also prove this analysis, where complexation took place in more acidic pH in which only the –COOH group has higher possibility to dissociate.

At higher pH more species occurred, as can be observed in the species distribution diagram. These species occurred due to further dissociation of ligand. For example in the complexation of Be^{2+} with DA, species were formed according to Eqs. (4) and (5).

$$Be^{2+} + DAH^{2-} \rightleftharpoons BeDAH \tag{4}$$

$$Be^{2+} + DA^{3-} \rightleftharpoons BeDA^- \tag{5}$$

The latter species formed was [BeL] which was formed by the binding of Be^{2+} with the fully dissociated ligand. The stepwise formation constant of these species expressed as $\log K_{ML}$, and the values are 13.54, 12.69, 13.68, 13.50 and 13.81 for CAT, SAL, DA, PA and GA, respectively. These species have higher stability constant value than other BeL–core species, indicating more stable species. A fully dissociated ligand has more negative charge hence it attract metal ion stronger. The [BeL] species of systems with DA, PA and GA have similar $\log K_{ML}$ values as the one with CAT. This indicates that [BeL] species are coordinated via the same binding group as that of CAT (chelate complex via two –OH groups or catecholate type).

It is expected that [BeL] will form a 5-membered chelate ring as catecholate-like complex rather than a 6-membered chelate ring salicylate-like complex, since 5-membered chelate ring has more stable and rigid structure than 6-membered chelate ring. Moreover, the 5-membered ring of the observed [BeL] complex involves only single bond atom resulting in more stable binding, while the 6-membered ring involves one single bond atom and one double bond atom. A 6-membered chelate ring will be more stable if all the atoms are double bonded [25,26]. The structures of [BeL] species were discussed further in the molecular modeling section later.

On the other hand, BeL_2–core species were formed by the ability of metal ions to bind multiple ligands to form ML_2 species. As presented in Table 1, the $\log\beta_{120}$ values of chelate complex between Be^{2+} ion and two fully dissociated ligands or $[BeL_2]$ species are 22.42, 22.56, 18.98, 23.14 and 20.35 for CAT, SAL, DA, PA and GA, respectively. The stepwise formation constant of $[BeL_2]$ species are represented as $\log K_{ML_2}$, where this value shows the strength of the second ligand to bind with the complex. It was shown that $\log K_{ML_2}$ is much lower than $\log K_{ML}$, indicating that the second ligand was bound not as strong as the first ligand. This phenomenon often occurred in the formation of $[BeL_2]$ species due to the bulkier species that caused a steric interaction between the ligands attached. However, overall $[BeL_2]$ species are more stable than [BeL] species as indicated by the higher $\log\beta_{120}$ values. The species distribution diagrams in Fig. 3 show that BeL_2 species is more likely to form at high pH. It is due to the fact that at high pH dissociation is easier to occur; hence the chance of chelation is higher.

As presented in Fig. 3, the hydrolysis of Be^{2+} happened in the CAT, DA and PA systems; where the $Be(OH)^+$ species existed at acidic pH (<7) and the neutral $Be(OH)_2$ species was predominantly found in the physiological pH (7.4). However, these two hydrolysis species of Be^{2+} were not found in the SAL and PA systems. This suggests that in the physiological pH, SAL and PA are able to form stronger binding with Be^{2+}. The other hydrolyzates such as $Be_2(OH)^{3+}$ and $Be_3(OH)_3^{3+}$ were not observed in the system indicating that the ligands were capable of inhibiting further hydrolysis of Be^{2+}.

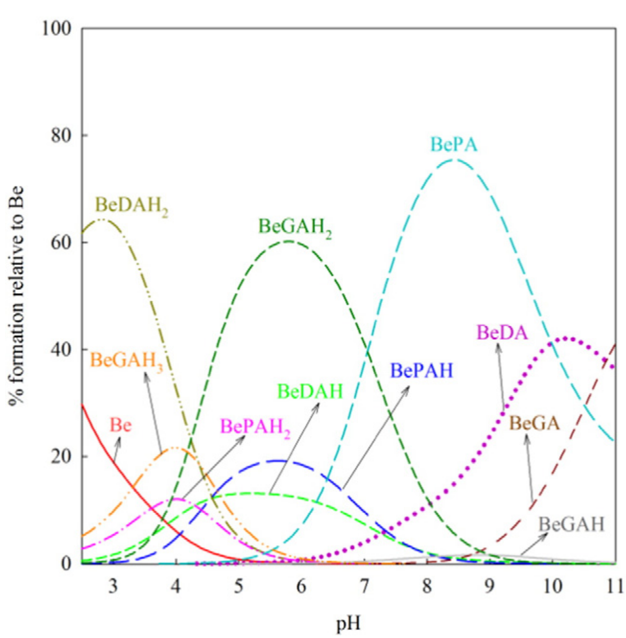

Fig. 5. Competition diagrams of DA, PA and GA as ligand to bind Be^{2+} in the mixed system, with a metal to ligand molar ratio of 1:2.5.

Table 3
Percentage of species formed in the mixed DA, PA and GA system.

Species	%max	pH	Species	%max	pH
Free Be	29.70	2.50	$BeGAH_3$	21.59	3.99
$BeDAH_2$	64.28	2.80	$BeGAH_2$	60.20	5.77
BeDAH	13.14	5.14	BeGAH	1.62	8.83
BeDA	42.08	10.24	BeGA	41.03	11.00
$BePAH_2$	12.06	3.99			
BePAH	19.15	5.60			
BePA	75.40	8.41			

3.2. Spectrophotometric measurement

The formation of the complex species were confirmed qualitatively by using UV–Visible spectrum measurement at wavelength 200 to 500 nm. The spectrum measurement were done for all the systems at pH 7 and 11. As shown in Fig. 4, the absorbance at range 200 to 250 occurred due to the aromatic ring of ligand. The shifting of the Be^{2+}–ligand spectrum compared to ligand spectrum was clearer observed at the basic pH 11. The shift indicated that the complex formation occurred in the system. Specifically, for (a) CAT system, initially the peak of ligand is showed at 284 nm, the formation of Be^{2+} complex cause shifting to 290 nm; (b) SAL system, the shifting is occur at 301 nm to 314 nm; (c) DA system, the formation of complex species caused the increasing of absorbance at 331 nm; (d) PA system, the shifting is occur at 305 nm to 313 nm; and (e) GA system, the shifting is occur at 273 nm to 285 nm.

3.3. Effectiveness of ligands

The effectiveness of the investigated ligand (DA, PA and GA) to bind Be^{2+} was analyzed from the ability of the ligand to form [BeL] species. When all three ligands are present in a system, they will compete with each other to bind the metal ion. Ligand which possesses stronger activity to attract and bind to the metal ion will form the most dominant species. As presented in competition diagram in Fig. 5, DA was the first ligand that bound Be^{2+}, followed by PA and GA to form species that were attached via –COOH group. This result is expected since the –COOH group of DA was tend to dissociate at more acidic pH compared to PA and GA [23]. While among these three ligands, PA is the most effective ligand to bind Be^{2+} since its species ([BePA]) was found in the highest concentration in the system. The maximum concentration of [BePA] species formed was 75.40% at pH 8.41, while the maximum concentration of [BeDA] and [BeGA] species was 42.08% at pH 10.24 and 41.03% at pH 11.0, respectively as shown in Table 3.

Table 4
Gibb's free energy ($\Delta_r G$) values of BeL–core complex calculated by DFT method with 6-311++G(d) basis set[a].

Model number	Ligand number				
	1	2	3	4	5
	CAT	SAL	DA	PA	GA
$\Delta_r G$ (hartree/particle)[b]					
(a)	−0.1372	−0.1129	−0.1118	−0.1245	−0.1240
(b)	−0.2582	−0.2489	−0.2432	−0.1797	−0.1822
(c)	–	–	−0.2745	−0.2628	−0.2624
(d)	–	–	−0.2797	–	−0.2936

[a] This table is related to Fig. 6; for example ligand number **1** (CAT) and model number **(a)** with $\Delta_r G$ −0.1372 represent model **1(a)** in Fig. 6.
[b] 1 hartree/particle = 2625.5 kJ·mol^{-1}.

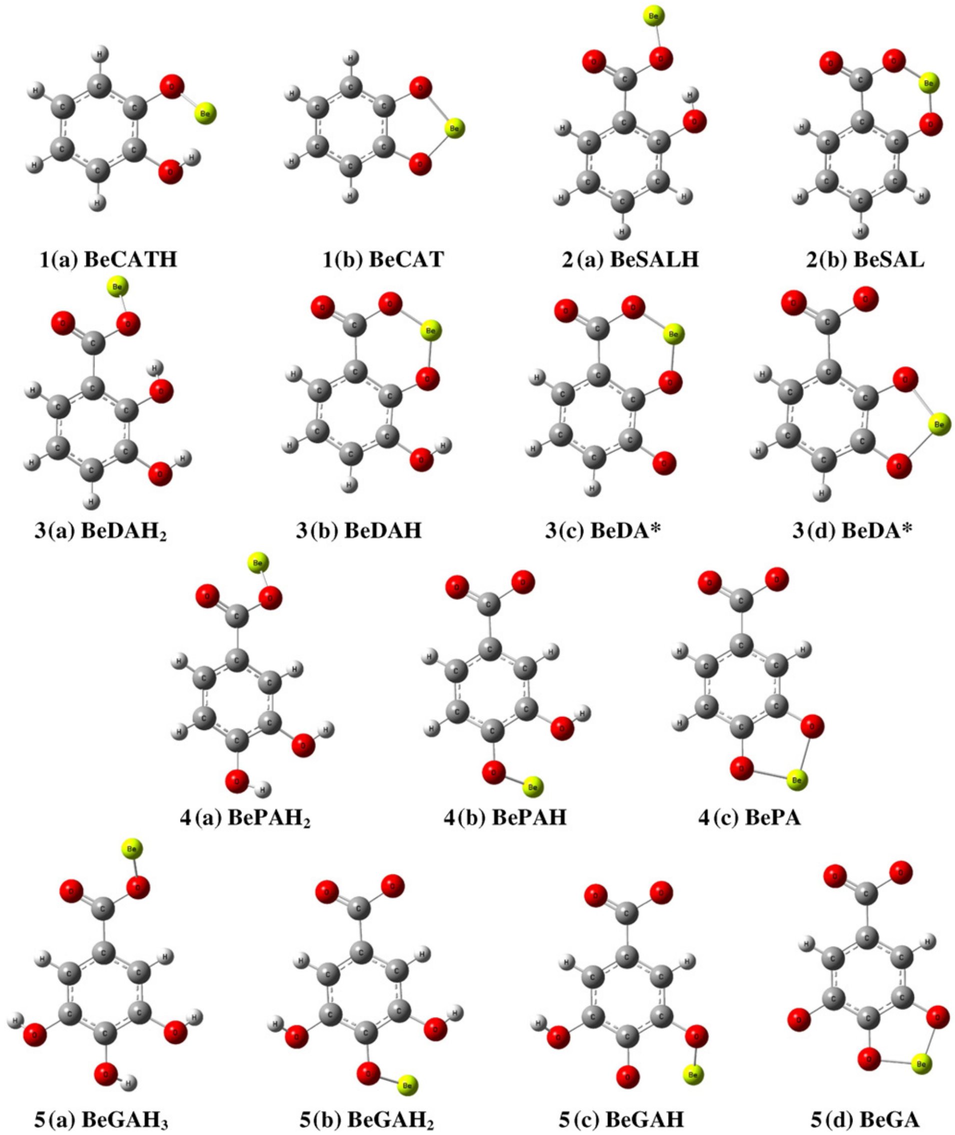

Fig. 6. Optimized structure of BeL–core species. *Model 3(c) is BeDA in salicylate manner and 3(d) is BeDA in catecholate manner.

3.4. Molecular modeling

The molecular structure of BeL–core species ([$BeLH_3$], [$BeLH_2$], [BeLH] and [BeL]) were calculated using density functional theory (DFT) method with B3LYP correlation and basis set of 6-311++G(d) by the Gaussian09W program, represented as Gibb's free energy of reaction ($\Delta_r G$). $\Delta_r G$ value was calculated by the following equation:

$$\Delta_r G = \Sigma G_{product} - \Sigma G_{reactant}. \tag{6}$$

The calculated $\Delta_r G$ are shown in Table 4 and optimized model of the species are shown in Fig. 6 where each ligand is symbolized by a number (**1** = CAT, **2** = SAL, **3** = DA, **4** = PA and **5** = GA).

$\Delta_r G$ values in Table 4 are proportional to the log*K* values obtained from potentiometric result. In all ligand systems, species with lower $\log K_{MLH_{(n-1)}}$ yielded less negative $\Delta_r G$ (−0.1372, −0.1129, −0.1118, −0.1245 and −0.1240 for CAT, SAL, DA, PA and GA, respectively where the structures are shown in Fig. 6 by models **1(a)**, **2(a)**, **3(a)**, **4(a)** and **5(a)**); compare to [ML] species which have higher $\log K_{ML}$ and yielded more negative $\Delta_r G$ (−0.2582, −0.2489, −0.2797, −0.2628 and −0.2936 for CAT, SAL, DA, PA and GA, respectively where the structures are shown in Fig. 6 by model **1(b)**, **2(b)**, **3(d)**, **4(c)** and **5(d)**). Based on the result for DA, the [BeDA] species prefer the catecholate manner than the salicylate manner (Fig. 6, model **3(c)** for salicylate manner and **3(d)** for catecholate manner), in which the catecholate manner complexes have more negative $\Delta_r G$ values.

4. Conclusion

The complexation of hydroxy aromatic antioxidants (DA, PA and GA) with Be^{2+} was investigated potentiometrically at $T = 310.15$ K and $I = 0.15$ mol·dm^{-3} NaCl. These antioxidants were capable of forming stable complexes with Be^{2+}. When the antioxidant (ligand) was fully dissociated, [BeL] species were formed by binding Be^{2+} through two OH groups in catecholate type with a $\log K_{ML}$ value of 13.68, 13.50 and 13.81 for DA, PA and GA, respectively. The DFT calculations well supported the [BeL] structure in catecholate binding mode with a $\Delta_r G$ value of −0.2797, −0.2628 and −0.2936 for DA, PA and GA, respectively. Among the three ligands, PA was shown to be the most effective ligand in preventing the hydrolysis of Be^{2+} especially in the physiological pH (7.4), followed by DA and then GA.

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