Complex Formation of Beryllium(II) with Salicylate and Hydroxide Ions in 1 mol dm^{-3} Sodium Perchlorate Aqueous Solution at 25°C

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The complex formation of Be^{2+} with salicylate (L^{2-}) and hydroxide ions was investigated at 25 °C in 1 mol dm^{-3} $NaClO_4$ by potentiometry using a glass electrode. The e.m.f. measurements were performed under the conditions $2.7 \leqslant -\log[H^+] \leqslant 8$, $0.002 \leqslant c_M \leqslant 0.01$ mol dm^{-3}, $0.002 \leqslant c_L \leqslant 0.015$ mol dm^{-3}, and $1 \leqslant c_L/c_M \leqslant 7$, where c_M and c_L denote the total concentrations of Be^{II} and salicylic acid, respectively. The e.m.f. data were explained with the three major species $[Be(HL)L]^-$, $[BeL]$, and $[BeL_2]^{2-}$ and at least one or even all of the four minor species $[Be(HL)]^+$, $[Be(HL)_2]$, $[Be(OH)L]^-$, and $[Be_3(OH)_3L_3]^{3-}$. The hydrolytic reactions of Be^{II} in 1 mol dm^{-3} $NaClO_4$, data on which were used for the analysis of the above beryllium(II)–salicylate–hydroxide system, were also studied by separate potentiometric titrations. It was found that $[Be_2(OH)]^{3+}$, $[Be_3(OH)_3]^{3+}$, and $[Be_6(OH)_8]^{4+}$ occur in 1 mol dm^{-3} $NaClO_4$ aqueous solution.

Based on the available equilibrium constants,[1–3] it is understood that beryllium(II), which has toxicological properties and is a trace element in natural waters, forms relatively stable complexes with salicylate anion. Salicylic acid (H_2L) has been regarded as one of the simplest model ligands for humic substances occurring in natural waters. So far, the equilibria between Be^{II} and salicylate have been interpreted in terms of the formation of a series of protonated ternary species $[Be(HL)_n]^{(2-n)+}$ (n = 1,[4] 1—3[5]), and of the chelates [BeL] and $[BeL_2]^{2-}$.[6–9] Other species such as ternary hydrolyzed complexes have not been reported. From this brief survey and an examination of the previous results, it may be said that a few data have been reported and the investigations have been performed under restricted conditions. Therefore, it would be worthwhile to obtain more data on this system. The present work was conducted at 25 °C in a 1 mol dm^{-3} $NaClO_4$ medium.

The hydrolysis of Be^{2+} ion, which must be taken into consideration in the analysis of this system, has been studied by many investigators. Potentiometric[10] and i.r. and Raman[11,12] investigations leave no doubt that the principal hydrolysis product in weakly acidic solutions more concentrated than 10^{-3} mol dm^{-3} is the trimer $[Be_3(OH)_3]^{3+}$. A dimer $[Be_2(OH)]^{3+}$, which is formed at low Z [average number of H^+ set free per Be^{II}, $([H^+] - c_H)/c_M$] is also firmly established.[10] On the other hand, it seems that there is still some ambiguity about the species formed at high Z. The species $Be(OH)_2$ was proposed by Kakihana and Sillén.[13] Mesmer and Baes[14] raised an objection to this and proposed $[Be_5(OH)_7]^{3+}$ or $[Be_6(OH)_8]^{4+}$, the formation of $[Be_6(OH)_8]^{4+}$ being supported by Lanza and Carpéni.[15] Ciavatta and Grimaldi[16] also denied the formation of $Be(OH)_2$ and proposed $[Be_2(OH)_2]^{2+}$ and $[Be_3(OH)_4]^{2+}$ at an elevated temperature (60 °C). Tsukuda *et al.*[17] carried out special potentiometric titration procedures and suggested that $Be(OH)_2$ readily formed by the addition of hydroxide ions is an 'oversaturated' complex and slowly changes to $[Be_6(OH)_8]^{4+}$ by releasing some hydroxide ions. This means that the polymerization reaction progresses so slowly that $Be(OH)_2$ is recognized as an equilibrium species at high Z values when titrations are carried out at normal speeds.

In the present work, prior to the investigation of the beryllium(II)–salicylic acid system, measurements of the hydrolytic reactions of Be^{II} were performed in 1 mol dm^{-3} $NaClO_4$ because of the lack of data in this medium and of some ambiguity about the species formed at high Z.

Experimental

Potentiometric Measurements.—The complex-formation equilibria were monitored by measuring the equilibrium hydrogen-ion concentration with a glass electrode. The e.m.f.s were measured for the cell of the type glass electrode | test solution | reference. The equilibrium hydrogen-ion concentration was calculated according to equation (1) where E_0 is a constant, which was determined *in situ* in a solution of known hydrogen-ion concentrations; E_j, the liquid-junction potential arising between the test solution and the salt bridge, was found to be approximated by $-55\,[H^+]$ mV.

$$| 1 \text{ mol dm}^{-3}\ NaClO_4 | 0.99 \text{ mol dm}^{-3}\ NaClO_4 + 0.01 \text{ mol dm}^{-3}\ AgClO_4 | Ag\text{–}AgCl$$

$$E = E_0 + 59.15 \log[H^+] + E_j \qquad (1)$$

For measuring the hydrolysis of Be^{II}, the total concentration of the latter, c_M, was kept constant during a titration, while the equilibrium hydrogen-ion concentration, $[H^+]$, was varied either by coulometric generation of H^+ or OH^- or by addition of H^+- or OH^--containing solution. Both forward (addition of OH^-) and backward (addition of H^+) titrations were carried out to ascertain the reversibility of the equilibria. For measuring the beryllium(II)–salicylic acid system, each titration was made at a constant c_L/c_M ratio, while the values of c_L (total concentration of salicylic acid) and c_M were decreased by dilution caused by addition of titrant. Forward titrations were carried out in the $-\log[H^+]$ range from 2.7 to 8. The precipitation of white products occurred at $-\log[H^+] \approx 6.2$ in solutions with $c_L/c_M \approx 1$.

Since on exposure to light the solutions containing salicylic acid were found to become yellow, the titration vessels were covered with aluminium foil. With this precaution no discolouration was observed during the titrations.

Apparatus.—A Beckman no. 39314 glass electrode was used in combination with an Ag–AgCl reference electrode prepared according to Brown,[18] which was set in a cell of the type described by Tsukuda *et al.*[17] The whole cell assembly was immersed in an oil thermostat at 25.00 ± 0.02 °C in a room thermostatted at 25 ± 1 °C. In measurements of the hydrolytic

Table 1. Error-square sums (U) and equilibrium constants ($\log \beta_{pq0}$) for hydrolysis of Be^{II} in 1 mol dm^{-3} $NaClO_4$ at 25 °C. The numbers in parentheses are standard deviations of the last decimal place

$[Be_2(OH)]^{3+}$	$[Be(OH)]^{+}$	$[Be_3(OH)_3]^{3+}$	$Be(OH)_2$	$[Be_2(OH)_2]^{2+}$	$[Be_3(OH)_4]^{2+}$	$[Be_6(OH)_8]^{4+}$	$[Be_6(OH)_9]^{3+}$	10^2U
−3.53(8)		−8.703(2)	−11.54(5)					8.03
−3.55(8)	< −10.2*	−8.703(3)	−11.54(6)					8.03
−3.49(7)		−8.706(5)		< −13.1*	−15.21(3)			7.02
−3.49(7)		−8.706(3)			−15.21(2)			7.02
−3.49(7)		−8.706(3)	< −17.0*		−15.21(7)			7.02
−3.52(7)		−8.700(2)				−26.82(2)		6.10
−3.55(8)		−8.706(2)			−15.7(2)	−27.02(6)		6.29
−3.56(8)		−8.700(2)					−32.81(2)	7.33
−3.51(8)		−8.706(3)			−15.30(7)		−33.5(3)	6.93
−3.1(1)		−8.71(1)			< −19.6*	−25.87(5)	< −37.1*	9.81
−3.1(1)		−8.70(1)				−25.83(4)	< −36.8*	9.82
−3.52(7)		−8.701(2)			< −19.9*	−26.82(4)		6.10

* Value is negligibly small.

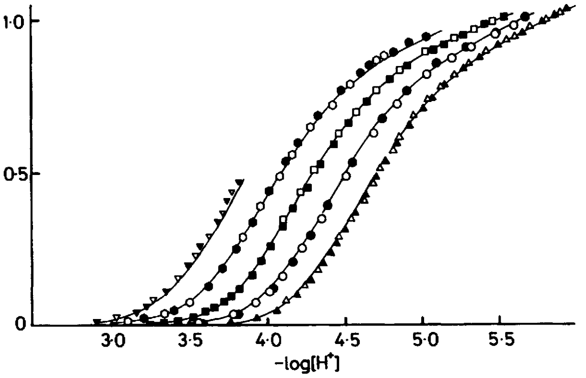

Figure 1. Plots of Z *vs.* $-\log [H^+]$. Filled symbols denote points from forward titrations and open symbols from backward titrations. For clarity all the data are not shown. The curves were calculated with the equilibrium constants given in Table 3. 10^3c_M/mol dm^{-3}: 2.489 (△), 4.996 (○), 10.00 (□), 20.00 (○), and 40.00 (▽)

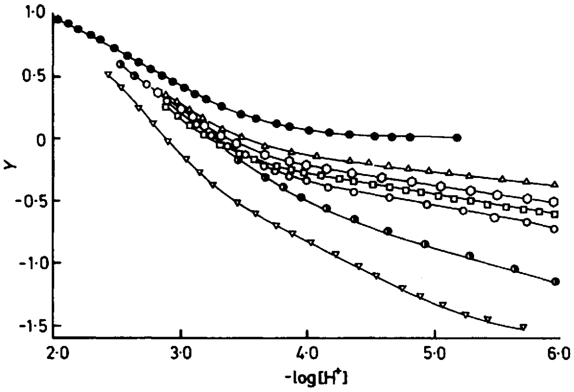

Figure 2. Plots of Y as a function of $-\log [H^+]$. For clarity only a fraction of the data is shown up to $-\log [H^+] = 6$. The data between $-\log [H^+] = 6$ and 8 are not plotted. The curves were calculated with the equilibrium constants given in Table 3. 10^3c_M/mol dm^{-3} (at initial point), 10^3c_L/mol dm^{-3} (at initial point): 0, 14.31 (●); 2.814, 13.19 (△); 2.814, 9.267 (○); 2.814, 6.056 (○); 2.815, 2.779 (◑); 5.080, 15.12 (□); and 11.70, 8.186 (▽)

reactions of Be^{II} the changes in e.m.f. were read with a model IOC-10 Ion-Meter from DKK (Tokyo), H^+ or OH^- being generated coulometrically by means of a Metrohm Coulostat E524 or added from a Metrohm E274 piston burette. For both e.m.f. reading and titrant addition in the beryllium(II)–salicylic acid system a model AUT-1 automatic titrator from TOA (Tokyo) was employed.

Reagents.—Beryllium perchlorate was prepared as follows. Beryllium oxide of analytical grade was heated for several hours with excess of perchloric acid so that it was converted into beryllium perchlorate. The undissolved beryllium oxide was filtered off with a glass filter. The beryllium perchlorate, which was recrystallized twice from water, was dissolved in redistilled water. The beryllium content of the stock solution was determined gravimetrically as BeO.[19] The perchlorate-ion concentration was determined by a cation-exchange method.

Sodium salicylate, Na(HL), of analytical grade was dried *in vacuo* over silica gel and used without further purification. Its purity checked potentiometrically was found to be in agreement with that expected from the weighed amount (within 0.2%). Sodium perchlorate was prepared by neutralizing an $HClO_4$ solution with recrystallized Na_2CO_3 as described by Sillén.[20] The stock solution was analyzed by evaporating a known amount of the solution at 120 °C and weighing the residue as $NaClO_4$. Sodium hydroxide solution was prepared from freshly filtered 50% NaOH solution and redistilled water freed from CO_2 by boiling.

Evaluation of the Composition and Equilibrium Constants of Hydroxo- and of Salicylate Complexes of Be^{II}.—(*a*) *Hydroxo complexes.* The potentiometric data are shown in Figure 1 in the form of Z *vs.* $-\log [H^+]$ in each series of c_M.

First, a graphical analysis based on the 'core + links' hypothesis[21] and the calculation of $\bar{p}$ and $\bar{q}$ values by the integration method[22] were performed to determine the composition and equilibrium constants of the hydrolysis species formed. The results suggested the formation mainly of $[Be_3(OH)_3]^{3+}$ ($-\log \beta_{3-30} = 8.73$) and of minor species the composition of which could not be identified. Thus, the least-squares computer calculations were applied to the determination of the composition and equilibrium constants of the minor species and to the refinement of the β_{3-30} value. The least-squares calculations were made to determine the most probable hydrolysis scheme involving the lowest number of species which would suffice to account for the experimental data and for the equilibrium constants of the species formed. The calculations were carried out by minimizing the error-square sum $U = \Sigma(Z - Z_{calc.})^2$, where $Z_{calc.} = -\Sigma\Sigma q\beta_{pq0}[Be^{2+}]^p[H^+]^q/c_M$. Several combinations of species previously reported to occur in aqueous solution were assumed. The results of the minimum error-square sums are summarized in Table 1.

(*b*) *Salicylate complexes.* The Y values, average number of H^+ bound per HL^-, $(c_H - [H^+])/c_L$, were calculated as a function of $\log [H^+]$. They are shown in Figure 2.

Table 2. Error-square sums (U) and equilibrium constants (log β_{pqr}) for beryllium(II)–salicylate complex formation in 1 mol dm^{-3} NaClO$_4$ at 25 °C: $p\mathrm{Be}^{2+} + q\mathrm{H}^{+} + r\mathrm{HL}^{-} \rightleftharpoons [\mathrm{Be}_p\mathrm{H}_q(\mathrm{HL})_r]^{(2p+q-r)+}$. The numbers in parentheses are standard deviations of the last decimal place

pqr							
1 0 1	1 0 2	1 −1 2	1 −1 1	1 −2 2	1 −2 1	3 −6 3	$10^{-1}U$
			−0.800(7)	−3.92(2)			2.54
1.56(10)			−0.76(1)	−3.88(2)			2.35
	3.85(9)		−0.79(1)	−3.90(2)			2.31
		0.64(7)	−0.88(1)	−3.91(1)			2.22
			−0.800(7)	−3.98(2)	−7.42(12)		2.34
			−0.80(1)	−3.95(2)		−15.33(17)	2.32
1.84(6)		0.88(5)	−0.83(2)	−3.83(2)			1.72
	4.09(6)	0.85(5)	−0.87(2)	−3.86(2)			1.72
		0.59(8)	−0.86(2)	−3.95(2)	−7.56(15)		2.09
		0.58(8)	−0.86(2)	−3.93(2)		−15.67(21)	2.09
1.55(21)	3.83(19)	0.88(5)	−0.85(2)	−3.84(2)			1.69
1.56(19)	3.77(21)	0.84(5)	−0.84(2)	−3.87(2)	−7.67(17)		1.61
1.55(20)	3.79(20)	0.84(5)	−0.84(2)	−3.85(2)		−15.85(24)	1.61
1.56(20)	3.78(21)	0.84(5)	−0.84(2)	−3.86(2)	−7.94(54)	−16.19(57)	1.60

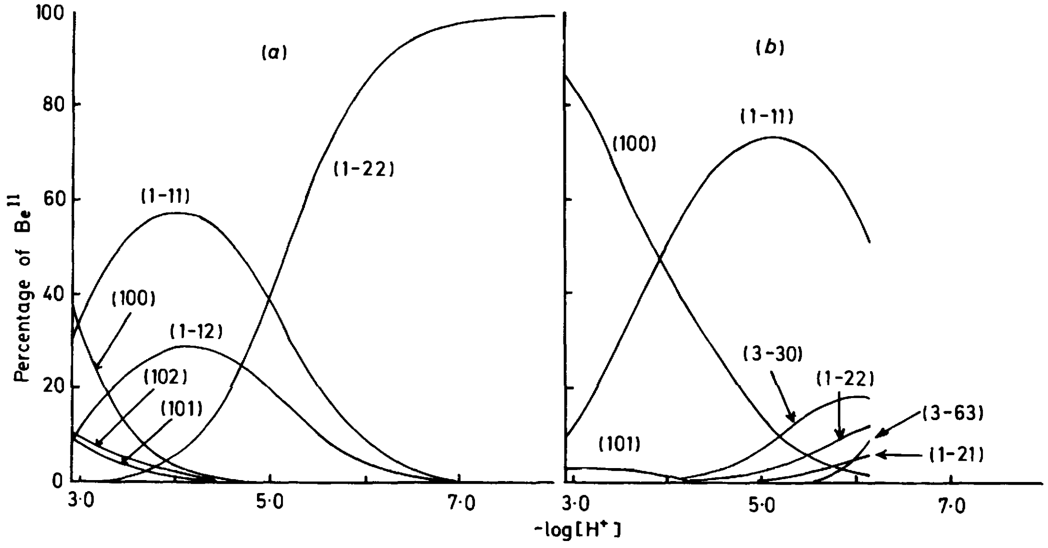

Figure 3. Calculated distributions of beryllium(II)–salicylate complexes at (*a*) $c_M = 2 \times 10^{-3}$, $c_L = 14 \times 10^{-3}$ mol dm^{-3} and (*b*) $c_M = 2 \times 10^{-3}$, $c_L = 2 \times 10^{-3}$ mol dm^{-3}

First, the carboxylic acidity constant of salicylic acid was evaluated by a graphical method[23] in which a normalized curve was fitted to the Y data with salicylic acid only in Figure 2. The acidity constant log β_{011} was 2.88 ± 0.01. The formation of dimeric species reported to occur in solutions of concentrated salicylic acid[24] was not observed in the present range of salicylic acid concentrations (c_L = 0.005 – 0.02 mol dm^{-3}). The phenolic acidity constant, which has been reported to be about −13.5 in log β units[1–3] could not be determined by the present potentiometric procedures with glass electrodes.

The data evaluation for the beryllium(II)–salicylate system was carried out with the least-squares computer program SCOGS[25] by minimizing the error-square sum $U = \Sigma(v - v_{\text{calc.}})^2$ where v = volume of titrant added (cm^3) and $v_{\text{calc.}}$ = that calculated using estimates of the equilibrium constants and the experimental [H$^+$] values. In the computer analysis the equilibrium constants for the hydrolysis of Be^{II} and the salicylic acid dissociation were fixed at the values determined in the separate titrations, while the equilibrium constants of a chosen ternary species (pqr) were allowed to vary systematically.

From Figure 2 it is seen that in the low −log [H$^+$] region (3.5—4.2), where HL$^-$ is predominant and no appreciable hydrolytic reaction of Be^{II} is expected, the Y values deviate significantly from the corresponding ones with salicylic acid in the direction of promotion of proton dissociation. This fact may indicate that species such as [BeL] and [BeL$_2$]$^{2-}$, the formation of which was reported previously, prevail. Thus, first, [BeL] and [BeL$_2$]$^{2-}$ were chosen as the probable species and subjected to least-squares calculations with the data in the restricted −log [H$^+$] region (3.5—4.2). The results suggested the existence of these two species. Then, the least-squares fit was performed on the whole data on the assumption of the occurrence of only these two species, and the results demonstrate that the two species should be accepted as the major ones. The value of the error-square sum calculated on the whole data for the [BeL] and [BeL$_2$]$^{2-}$, (1 −1 1) and (1 −2 2) species, respectively, is given in Table 2, along with their β_{pqr} values. Next, additional species (pqr) were searched for. The choice of these was made on the assumptions that Be^{II} is four-co-ordinated and that as for ternary polynuclear ($p \geqslant 2$) hydroxo complexes they should consist of binary hydroxo complexes, *i.e.* [Be$_2$(OH)]$^{3+}$, [Be$_3$(OH)$_3$]$^{3+}$, and [Be$_6$(OH)$_8$]$^{4+}$. In combination with the (1 −1 1) and (1 −2 2) species, those such as (103), (1 − 31), (2 − 12), (2 − 21), (2 − 32), (3 − 41), (3 − 52), and (6 − 81) made little contribution to the lowering of the error-square sum for each three-species scheme, and the β_{pqr} values of the latter species decreased to such an extent that these species had to be rejected. In Table 2 are summarized the values of the error-square sums and the equilibrium constants calculated for different combinations of species which resulted in lower error-square sums than the combination of only the (1 − 11) and (1 − 22).

Results and Discussion

Table 1 shows that the scheme involving $[Be_2(OH)]^{3+}$, $[Be_3(OH)_3]^{3+}$, and $[Be_6(OH)_8]^{4+}$ gives rise to the least error-square sum of those chosen. The systematic deviations from the experimental data, $Z - Z_{calc.}$, for $Z > 0.7$ were examined for both $[Be_2(OH)]^{3+}$–$[Be_3(OH)_3]^{3+}$–$[Be_6(OH)_8]^{4+}$ and $[Be_2(OH)]^{3+}$–$[Be_3(OH)_3]^{3+}$–$[Be_3(OH)_4]^{2+}$–$[Be_6(OH)_8]^{4+}$ which resulted in the second lowest error-square sum. It seemed that the systematic deviations were slightly less for the former scheme. We conclude that $[Be_3(OH)_3]^{3+}$ is the dominating species; $[Be_2(OH)]^{3+}$ is formed at lower Z and $[Be_6(OH)_8]^{4+}$ at higher Z. Our conclusion is consistent with those made for 1 mol kg^{-1} NaCl[14] and 3 mol dm^{-3} $LiClO_4$.[17] The formation constants for the $[Be_2(OH)]^{3+}$ and $[Be_3(OH)_3]^{3+}$ complexes in 1 mol dm^{-3} $NaClO_4$ are smaller than the corresponding ones in 3 mol dm^{-3} $NaClO_4$.[26]

From Table 2, it is apparent that the equilibrium constant and its standard deviation for each species do not appreciably vary with differing combinations of species, and that the combination of all the seven species gives rise to the least error-square sum. These results are consistent with the formation of the three major species (1 − 12), (1 − 11), and (1 − 22) and at least one or even all of the four minor species (101), (102), (1 − 21), and (3 − 63).

The amounts of the seven species at two different c_L/c_M ratios were calculated by using the equilibrium constants in Table 2, and are plotted as a function of $-\log[H^+]$ in Figure 3. It is seen that at $c_L/c_M = 7$ the (1 − 11) and (1 − 12) species are predominant at lower $-\log[H^+]$ and the (1 − 22) species at higher $-\log[H^+]$, and that the (101) and (102) species are formed in small amounts at low $-\log[H^+]$. The (1 − 21) and (3 − 63) species do not occur in detectable quantities. At $c_L/c_M = 1$ the (1 − 11) species is also prevalent and the (1 − 21) and (3 − 63) species are minor in the $-\log[H^+]$ range up to about 6.2, beyond which e.m.f. titrations were impossible due to precipitation. It is apparent from Figure 3 that the large standard deviations of the equilibrium constants for the (101), (102), (1 − 21), and (3 − 63) species should be ascribed to their low concentrations. Thus, we propose the formation of (1 − 11), (1 − 12), and (1 − 22) as major species and of minor species such as (101) and (102) at low $-\log[H^+]$ and (1 − 21) and (3 − 63) at high $-\log[H^+]$ under the present experimental conditions. However, the identification of the (1 − 21) and (3 − 63) species may not be conclusive because of the precipitation at low c_L/c_M and high $-\log[H^+]$ where hydrolyzed species like them may become predominant.

The two species (1 − 11) and (1 − 22) occurring at low $-\log[H^+]$ may be chelates within which both the carboxyl and hydroxyl groups co-ordinate to Be^{II}, and these can be written as [BeL] and $[BeL_2]^{2-}$, respectively. The species (1 − 12) formed at high c_L/c_M ratio, and at low $-\log[H^+]$ where no appreciable hydrolysis of Be^{II} is expected, could be $[Be(HL)L]^-$. The species (1 − 21) which appears at low c_L/c_M and high $-\log[H^+]$ may be a hydrolyzed species, which could be written as $[Be(OH)L]^-$. As was assumed in the search for a third new species, the (3 − 63) species corresponds to $[Be_3(OH)_3L_3]^{3-}$.

Table 3. Equilibrium constants (β_{pqr}) for hydroxo and salicylate complexes of Be^{II} in 1 mol dm^{-3} $NaClO_4$ at 25 °C. The numbers in parentheses are standard deviations of the last decimal place

Species proposed	*pqr*	log β_{pqr}
$[Be_2(OH)]^{3+}$	2 − 1 0	−3.52(7)
$[Be_3(OH)_3]^{3+}$	3 − 3 0	−8.700(2)
$[Be_6(OH)_8]^{4+}$	6 − 8 0	−26.82(2)
H_2L	0 1 1	2.88(1)
$[Be(HL)]^+$	1 0 1	1.56(21)
$[Be(HL)_2]$	1 0 2	3.78(21)
$[Be(HL)L]^-$	1 − 1 2	0.84(8)
[BeL]	1 − 1 1	−0.84(2)
$[BeL_2]^{2-}$	1 − 2 2	−3.86(2)
$[Be(OH)L]^-$	1 − 2 1	−7.9(6)
$[Be_3(OH)_3L_3]^{3-}$	3 − 6 3	−16.2(6)

The final results are summarized in Table 3. A new major species found in the present work is protonated $[Be(HL)L]^-$. The hydrolyzed species $[Be(OH)L]^-$ and $[Be_3(OH)_3L_3]^{3-}$, the existence of which was not reported previously, were also detected, but, as was pointed out above, their presence is ambiguous.

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