

The Complex Equilibria between Be^{2+} Ions and 4- or 6-Hydroxysalicylic Acid in 0.5 M NaClO_4 Medium

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The beryllium(II) complex formation with 4- and 6-hydroxysalicylic acids (H_3L) in aqueous 0.5 M sodium perchlorate solution at 25 °C has been studied by a potentiometric method. The data indicate the formation of the species BeHL and $\text{BeH}_2\text{L}_2^{2-}$ at pH values lower than 7, and BeHL_2^{3-} and BeL_2^{4-} at pH values higher than 7 in solutions of Be^{2+} ions and 4-hydroxysalicylic acid. In the acidic region, moreover, 6-hydroxysalicylic acid also forms a binuclear complex compound, Be_2L^+ , when an excess of Be(II) is present. In the alkaline pH region (up to pH 11) the only significant reaction in the beryllium–6-hydroxysalicylic acid system is the dissociation of $\text{BeH}_2\text{L}_2^{2-}$ into BeHL_2^{3-} .

In a previous paper we reported the complex equilibria between Be^{2+} ions and 5-hydroxysalicylic acid.¹ We now extend these studies on the reactions between Be^{2+} ions and derivatives of salicylic acid to 4-hydroxy- and 6-hydroxysalicylic acids.

All the data refer to an aqueous solution 0.5 M with respect to the total perchlorate ion concentration and 25 °C.

EXPERIMENTAL

Reagents. 4-Hydroxysalicylic (2,4-dihydroxybenzoic) acid and 6-hydroxysalicylic (2,6-dihydroxybenzoic) acid were reagents from Fluka AG, and they were recrystallized from water before use.

Be^{2+} solutions were prepared from the corresponding nitrate (E. Merck AG).

Apparatus. The potentiometric titrations were carried out automatically with a Radiometer digital titration system DTS 633 (modified in this laboratory²), consisting of an autoburette ABU 13, a pH meter PHM 64, and a digital titrator TTT 61. A

Beckman N 40495 glass electrode was used as an indicator electrode with a calomel reference electrode, in which the electrolyte was 0.5 M NaCl solution. The electrode system was calibrated with standardized solutions of HCl , acetic acid and NaOH (all these buffer solutions were 0.5 M with respect to NaClO_4) by means of the following Nernst equation

$$E = E^\circ + 59.16 \log [\text{H}^+] + E_j \quad (1)$$

The determination of the liquid junction potentials, E_j , is described elsewhere.³

Methods. During the titrations for resolving the stability constants of the beryllium complexes, the total concentrations of beryllium, C_M , and the ligand acid, C_L , were kept constant. The ratio $C_L:C_M$ was varied systematically between 0.7 and 10 in the different titrations. The free hydrogen ion concentration, $[\text{H}^+]$, was decreased by adding sodium hydroxide to the test solutions. The reversibility of the equilibrium systems was also tested by reversing some of the titrations by introducing perchloric acid into the alkaline solutions of Be^{2+} ions and 4- or 6-hydroxysalicylic acid.

Because of the poor solubility of hydroxysalicylic acids, the total concentrations of beryllium and ligands were varied between 0.001 and 0.030 M.

The buffer solutions, the solutions to be titrated and the titrant were all made 0.5 M with regard to NaClO_4 .

Calculations. The equilibrium constants were calculated as overall stability constants [$\beta_{qpr} = K(q\text{M}^{2+} + \text{H}^+ + r\text{L}^{3-} = \text{M}_q\text{H}_p\text{L}_r^{2q+p-3r})$] with the programme SCOGS⁴ on a Univac 1100/20 computer.

The hydrolysis of Be^{2+} ions was taken into account by assuming the following constants $\log \beta_{3,-3,0} = -8.81$, $\log \beta_{2,-1,0} = -3.24$, and $\log \beta_{1,-2,0} = -11.0$.⁵

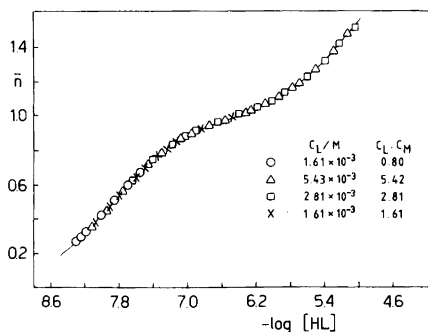


Fig. 1. Experimental values of \bar{n} versus $-\log [HL]$ calculated from a few different titrations of beryllium(II) ions and 4-hydroxysalicylic acid with NaOH solution ($pH < 7$).

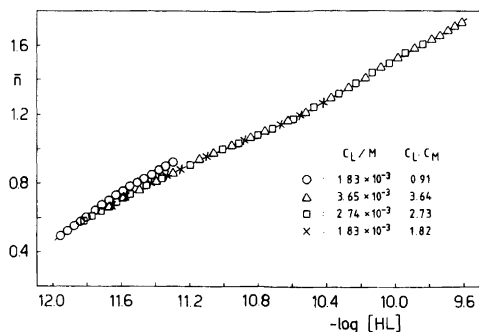


Fig. 2. Experimental values of \bar{n} versus $-\log [HL]$ calculated from a few titrations of beryllium(II) ions and 6-hydroxysalicylic acid with NaOH solution ($pH < 7$).

TREATMENT OF DATA

The equilibria between Be^{2+} and 4-hydroxysalicylic acid. Part of the potentiometric data are presented as an $\bar{n}(-\log [HL])$ plot in Fig. 1 where the average number of salicylates bound per beryllium is denoted by \bar{n} . The points have been calculated from the titration steps where pH is under 7. As it can be seen from this figure, \bar{n} seems to be a function of $[HL]$ even in the solutions where an excess of the metal ions is present, thus indicating the formation of the stepwise complexes $Be(HL)_r$. In the alkaline pH region the computer analyses indicate a dissociation of the complex $BeH_2L_2^{2-}$ into $BeHL_2^{3-}$ and BeL_2^{4-} . Because of the formation of precipitates, titrations with $C_L:C_M$ ratios smaller than 1.5 were not possible in the alkaline solutions, and we were not able to determine the stability constant of the complex BeL^- .

The equilibria between Be^{2+} and 6-hydroxysalicylic acid. In this case too, the data were visualized by making a Bjerrum plot $\bar{n}(-\log [HL])$ over the points in the acidic pH region. It can be seen from this plot (Fig. 2) that for quotients $C_L:C_M > 1$ the function $\bar{n}(-\log [HL])$ seems to be independent of C_L and C_M , thus indicating the formation of a series of the mononuclear metal complexes $Be(HL)_r$. However, when the ratio $C_L:C_M$ is smaller than 1, the function seems to depend on both $[HL]$ and C_M , thus indicating the possible formation of one or more polynuclear complex compound among the $Be(HL)_r$ species. The computer analyses then showed the formation of the complex Be_2L^+ in solutions where $C_L:C_M < 1$.

In the alkaline pH region the only detected reaction was the dissociation of the compound $BeH_2L_2^{2-}$ into $BeHL_2^{3-}$ in the solutions where $C_L:C_M \geq 2$ and $7 < pH < 11.5$.

Table 1. The protonation constants used in the calculations and the stability constants of the beryllium(II) complexes of 4-hydroxysalicylic (1), 5-hydroxysalicylic (2) and 6-hydroxysalicylic (3) acids at $I=0.5$ ($NaClO_4$) and $25^\circ C$. $\log \beta_{011} = pK_{a3}$, $\log \beta_{021} - \log \beta_{011} = pK_{a2}$ and $\log \beta_{031} - \log \beta_{021} = pK_{a1}$. The values in parentheses are the standard deviations.

Ligand acid	$\log \beta_{011}$	$\log \beta_{021}$	$\log \beta_{031}$	$\log \beta_{052}$	$\log \beta_{062}$	Refs.
(1)	13.373	21.928	25.046	47.17	50.556	(6)
(2)	12.742	22.737	25.468			(6)
(3)	13.283	25.854	27.050			(6)
Ligand acid	$\log \beta_{111}$	$\log \beta_{122}$	$\log \beta_{201}$	$\log \beta_{112}$	$\log \beta_{102}$	Refs.
(1)	20.238(0.001)	37.933(0.006)		29.018(0.025)	19.803(0.010)	This work
(2)	21.839(0.002)	41.347(0.004)		31.409(0.017)	20.972(0.012)	(1)
(3)	25.203(0.004)	48.528(0.006)	25.089(0.025)	36.765(0.040)		This work

The best stability constants obtained along with the standard deviations are presented in Table 1. The experimental data (\bar{n} , pH, C_L and C_M) are available from the authors.

DISCUSSION

The complex formation equilibria between 4-hydroxysalicylic acid and Be^{2+} ions closely resemble those of 5-hydroxysalicylic acid and Be^{2+} ions in 0.5 M aqueous NaClO_4 solutions, as expected. In the acidic pH region two successive complexes, BeHL and $\text{BeH}_2\text{L}_2^{2-}$, are formed, and the data obtained provide no evidence for the formation of polynuclear compounds even in solutions where an excess of the metal ions is present. Also, the reactions of these two beryllium systems are practically similar in alkaline solutions when an excess of the ligand is present: the species BeHL_3^{3-} and BeL_2^{4-} are formed *via* the dissociation of the compound $\text{BeH}_2\text{L}_2^{2-}$.

The complex formation equilibria with 6-hydroxysalicylic acid follow a different pattern. In the acidic pH region besides the complexes BeHL and $\text{BeH}_2\text{L}_2^{2-}$ the species Be_2L^+ is formed when an excess of the metal ions is present. One can expect that the coordination of Be^{2+} with 6-hydroxysalicylic acid in the complex BeHL is similar to that in the 1:1 beryllium complex of salicylic acid (Fig. 3). In the case of the polynuclear species Be_2L^+ , two six-membered chelate rings are probably formed, and the two oxygen atoms in the carboxyl group take part in the bonding. In the case of 4-hydroxy- and 5-hydroxysalicylic acids no polynuclear compounds were detected, which indicates

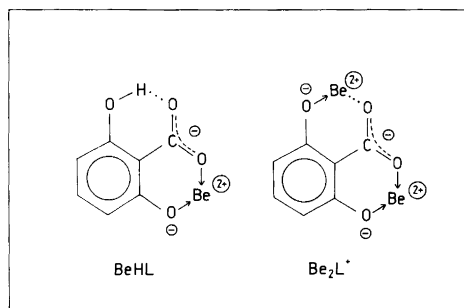


Fig. 3. The likely structures of the complexes BeHL and Be_2L^+ of 6-hydroxysalicylic acid.

that the isolated hydroxyl groups do not coordinate to beryllium under the conditions studied.

The dissociation of the compound $\text{BeH}_2\text{L}_2^{2-}$ in the beryllium–6-hydroxysalicylic acid system is less extensive than in the 4- and 5-hydroxysalicylic acid systems, and it occurs at higher pH values. The formation of the deprotonated species BeL_2^{4-} in solutions of 6-hydroxysalicylic acid is so slight at pH values lower than 11.5 that we have been unable to determine the stability of this complex. The poor formation of the compounds BeHL_3^{3-} and BeL_2^{4-} of 6-hydroxysalicylic acid in comparison with the corresponding compounds of 4-hydroxy- and 5-hydroxysalicylic acids can be explained with the intramolecular hydrogen bonds between the carboxyl and hydroxyl groups (Fig. 3). In 4- and 5-hydroxy derivatives the isolated hydroxyl groups are located so far from the carboxyl group that no hydrogen bonds are formed, and there is thus no increased difficulty in the dissociation of the proton in the hydroxyl group.

The stability of the beryllium complexes decreases in the order 6-hydroxysalicylic acid > 5-hydroxysalicylic acid > 4-hydroxysalicylic acid, which coincides with the increasing overall acidity of the ligand acids. Judging from the ratios k_{111}/k_{122} [$k_{111} = K(\text{M}^{2+} + \text{HL}^{2-} = \text{MHL})$ and $k_{122} = K(\text{MHL} + \text{HL}^{2-} = \text{MH}_2\text{L}_2^{2-})$], which are all between 1.9 and 2.5 log units for the present complexes, the hydroxyl group in the carbon C-4, C-5 or C-6 position has a similar effect on the successive beryllium complex formation of 4-, 5- and 6-hydroxysalicylic acids.

The beryllium(II) complex formation of 4-hydroxy- and 5-hydroxysalicylic acids depends on the free hydrogen ion and ligand anion concentrations, and that of 6-hydroxysalicylic acid on the metal ion concentration as well. If, however, there is an excess of the ligand acid present in the solutions, all the beryllium systems can be presented as a function of $[\text{H}^+]$ and $[\text{L}^{3-}]$. Figs. 4 and 5 show the formation of various beryllium species three-dimensionally for 4-hydroxy- and 6-hydroxysalicylic acids in the pH and $-\log [\text{L}]$ ranges studied and assuming that there is an excess of the ligand present. For the sake of clarity, the formation of each species is presented in a separate figure.

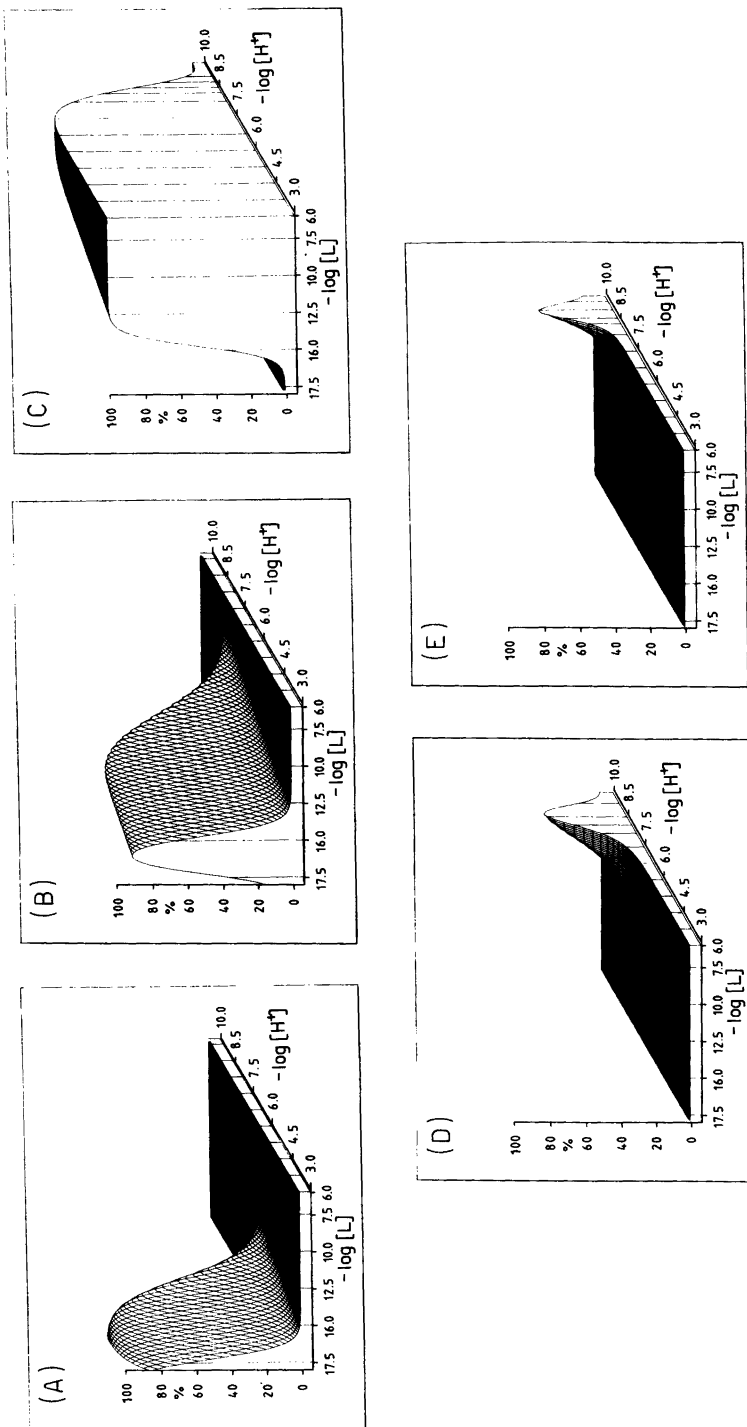


Fig. 4. Three-dimensional representation of the formation of the different beryllium species Be^{2+} (A), $BeHL$ (B), $BeHL_2^{2-}$ (C), $BeHL_3^{3-}$ (D) and BeL_4^{4-} (E) with 4-hydroxysalicylic acid; The ratio $[species]/C_M$ as a function of $-\log [L]$ and $-\log [H^+]$.

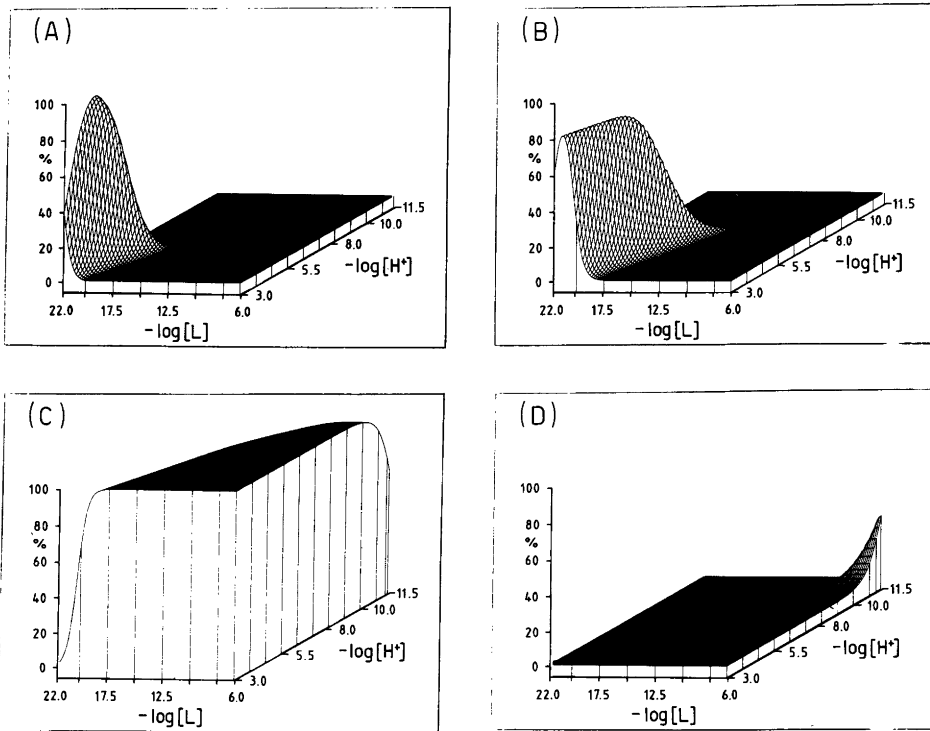


Fig. 5. Three-dimensional representation of the formation of the different beryllium species Be^{2+} (A), BeHL (B), $\text{BeH}_2\text{L}_2^{2-}$ (C) and BeHL_3^{3-} (D) with 6-hydroxysalicylic acid.

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