

Complex Formation Equilibria of Some Aliphatic α -Hydroxycarboxylic Acids. 3. A Study of Beryllium(II) Complexes

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Complex formation equilibria of beryllium(II) with five aliphatic α -hydroxycarboxylic acids, viz. glycolic (HL), lactic (HL), 2-hydroxyisobutyric (HL), L(+)-tartaric (H₂L) and citric (H₃L) acids, were studied by means of potentiometric (glass electrode) titrations at 25 °C in an ionic medium of 0.5 M NaClO₄. The titrations were performed in a pH range in which precipitation did not occur. Glycolic and 2-hydroxyisobutyric acid complexation with beryllium(II) are described by the formation of three rather weak complexes, namely BeL⁺, BeL₂ and Be₃(OH)₃L²⁺. Lactic acid was not found to form BeL₂ species. The equilibrium model for tartaric acid constitutes of the three complexes mentioned above together with two deprotonated complexes Be(H₋₁L)₂⁴⁻ and Be₃(OH)₃(H₋₁L). Citric acid was found to form also protonated and binuclear species prior to the formation of hydrolyzed complexes. The *p,q,r* analysis gave the following set of complexes: BeL⁺, BeL₂⁴⁻, Be₂L₂²⁻, BeHL, Be₂H₋₂L₂⁴⁻ and Be₂H₋₃L₂⁵⁻. The stability constants for these complexes with their standard deviations are reported.

Aliphatic α -hydroxycarboxylic acids are naturally occurring compounds which are important in many branches of science. The chemistry of natural waters can be studied by investigating the properties of the simple hydroxycarboxylic acids. Plant roots produce and release citric and tartaric acids, which they use to take up trace metals from the soil. The metal speciation in the presence of these acids is important, for instance, in understanding how the soil pH affects the chemical forms of metals and thus their availability to plants.

The beryllium content of the earth's crust is estimated to be 2–3.5 mg/kg.¹ The most important mineral of beryllium is beryl, Be₃Al₂(SiO₃)₆. Owing to its high stiffness to weight ratio beryllium is extensively used in several lightweight metal alloys. Its major uses are in the nuclear, aerospace and electronics industries.² Beryllium is regarded as the most toxic non-radioactive element. The most serious hazard to health is inhalation of dusts of beryllium compounds causing the disease called berylliosis.³ Beryllium in water soluble compounds is reported to be toxic to plants. Calcium uptake decreases and phosphorus uptake increases in the presence of beryllium.⁴

The Be²⁺ ion is tetrahydrated in acidic aqueous solu-

tion. Because of the small size of the ion beryllium cannot expand its coordination number to six like other members of the alkaline-earth metals. The Be²⁺ is extensively hydrolyzed at pH > 3. Beryllium(II) hydrolysis has been studied by several authors,^{5–10} and [Be₃(OH)₃]³⁺ has been confirmed to be the main species. The structure of this trimer is proposed to be a six-membered ring in which the beryllium ions are linked by hydroxyl bridges.⁶ A dimer [Be₂(OH)]³⁺ is also firmly established. Attempts to find the minor species formed prior to precipitation of Be(OH)₂ have been far more controversial. Many different hydrolysis products have been proposed for this region, viz. Be(OH)₂,^{5,6,8,10} [Be₅(OH)₆]⁴⁺,⁸ [Be₅(OH)₇]³⁺,⁷ and [Be₆(OH)₈]⁴⁺.^{8,9} The equilibrium constants determined by Bertin *et al.*⁵ were used in this work.

Complex formation of beryllium(II) with aliphatic α -hydroxycarboxylic acids has not been studied comprehensively.^{11,12} Duc and Thomas-David^{13,14} have investigated 2-hydroxyisobutyric and tartaric acid systems. For 2-hydroxyisobutyric acid the equilibrium model they reported constitutes of four complexes, viz. BeL⁺, BeL₂, Be(H₋₁L) and Be₃(OH)₃L₃. The system of beryllium(II) with (+)-tartaric acid was described by the following complexes: BeL, BeL₂²⁻, Be(H₋₁L)₂⁴⁻, Be₃(OH)₃L⁺ and Be₃(OH)₃(H₋₁L). According to the studies of Vanni

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and Gennaro¹⁵ the complex formation of beryllium(II) with citric acid is more complicated than that of tartaric acid. In addition to the mononuclear and protonated complexes they described the system by the $\text{Be}_2\text{L}_2^{2-}$ species with several hydrolyzed complexes.

The aim of this series of investigations is to study the complexing tendencies of five aliphatic α -hydroxycarboxylic acids [glycolic, lactic, 2-hydroxyisobutyric, L(+)-tartaric and citric acids] in comparable experimental conditions in order to evaluate their applicability for use in detergents and fertilizers. Also, the chemistry of natural waters is of interest. In the previous parts of this series we reported the protonation equilibria and complex formation of calcium(II), magnesium(II) and copper(II).^{16,17} In this third part the complex formation of beryllium(II) is studied.

Experimental

Chemicals and methods. A stock solution of beryllium(II) was prepared from $\text{Be}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Merck). The beryllium concentration was determined by titration with 0.1 M NaOH solution after the solution had been passed through a cation exchanger.

The hydroxycarboxylic acids were commercially available and used without further purification [glycolic acid (2-hydroxyethanoic acid, $\text{C}_2\text{H}_4\text{O}_3$, HL, Fluka AG), lactic acid (2-hydroxypropanoic acid, $\text{C}_3\text{H}_6\text{O}_3$, HL, Merck)], 2-hydroxyisobutyric acid (2-hydroxy-2-methylpropanoic acid, $\text{C}_4\text{H}_8\text{O}_3$, HL, Riedel-deHaen AG), L(+)-tartaric acid [L(+)-2,3-dihydroxybutanedioic acid, $\text{C}_4\text{H}_6\text{O}_6$, H_2L , Merck and citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid, $\text{C}_6\text{H}_8\text{O}_7$, H_3L , Merck)]. The concentrations of the aqueous solutions of the ligand acids were determined by potentiometric titration with a standard solution of NaOH.

The complex formation equilibria were studied by potentiometric (glass electrode) titrations at $25.0 \pm 0.1^\circ\text{C}$ in an ionic medium of 0.5 M NaClO_4 . The preparation of other solutions, apparatus and method used, including the procedure to calibrate the glass electrode, are fully described in Ref. 16. The concentrations of beryllium (B) and ligand acid (C) in the titrations performed for the present investigation are presented in Table 1. This table also summarizes the total number of equilibrium data

collected in each system, together with the pH range of the titrations covered. The pH range in each titration was restricted by the formation of white precipitate.

Data treatment. The beryllium(II) complexes of the hydroxycarboxylic acids were calculated from the potentiometric data with the computer program LETAGROP.^{18,19} The analysis of the experimental results was started with a calculation of the experimental $Z_{A/C}$ for each point of a titration. This value is defined as the average number of protons bound to each ligand [eqn. (1)]:

$$Z_{A/C} = [H - (h - k_w h^{-1})] / C \quad (1)$$

where H denotes the total concentration of the protons. The curves $Z_{A/C}$ vs. $-\log h$ were used to visualize the formation of hydrolyzed complexes. Also, calculated curves representing the complexes and corresponding stability constants obtained in this work were included. In order to find out the pH range where the possible hydrolyzed complexes were formed, \bar{n} vs. $\log[L]$ curves were plotted. Here \bar{n} represents the average number of ligands bound to metal.

The equilibrium reactions in a three component system can be described by the general relation (charges are omitted):



In some cases a search for the complex model and calculation of the corresponding stability constants were performed by splitting the experimental data. The binary Be_qL_r complexes and possible protonated complexes were calculated in the pH range where no hydrolyzed complexes existed. Finally, the $\text{Be}_q\text{H}_{p-q}\text{L}_r$ species were searched by the p,q,r analysis assuming the previously calculated values to be known. The aim of the analysis was to find a complex or complexes giving the lowest error squares sum $U = \sum (H_{\text{calc}} - H_{\text{exp}})^2$ by testing different p,q,r combinations. The LETAGROP calculations also gave the standard deviations $3\sigma(\log \beta_{p,q,r})$. The program SOLGASWATER²⁰ was used to calculate distribution diagrams for the equilibrium systems. The hydrolysis of Be^{2+} was taken into account in the calculations by using the following constants as fixed parameters in the least-squares refinements $\log \beta_{-3,3,0} = -8.81$, $\log \beta_{-1,2,0} =$

Table 1. The experimental conditions of the solutions studied in this work together with the total number of data collected in each system.

	Glycolic acid	Lactic acid	2-Hydroxyisobutyric acid	(+)-Tartaric acid	Citric acid
No. of titrations	7	7	7	7	7
No. of data points	365	324	302	304	368
Concentration of ligand (C)/M	0.007–0.016	0.008–0.016	0.007–0.015	0.005–0.011	0.003–0.008
Concentration of beryllium (B)/M	0.003–0.011	0.003–0.011	0.003–0.011	0.003–0.007	0.002–0.005
C/B	0.7–4.9	0.7–5.2	0.6–4.8	0.7–4.1	0.6–4.1
pH range	2.7–6.3	2.6–6.3	2.7–6.2	2.4–6.3	2.5–9.0

Table 2. Protonation constants used in the calculations.¹⁶

Ligand	log β _{1,0,1}	log β _{2,0,1}	log β _{3,0,1}
Glycolic acid	3.568 ± 0.003		
Lactic acid	3.45 ± 0.03		
2-Hydroxyisobutyric acid	3.760 ± 0.006		
(+)-Tartaric acid	3.724 ± 0.004	6.471 ± 0.004	
Citric acid	5.317 ± 0.007	9.464 ± 0.007	12.296 ± 0.008

Table 3. Stability constants of beryllium(II) complexes of glycolic, lactic and 2-hydroxyisobutyric acids (0.5 M NaClO₄, 25 °C).

Ligand	Formula	log(β ± 3σ)	Ref.
Glycolic acid	BeL ⁺	1.05 ± 0.02	This work
	BeL ₂	2.85 ± 0.01	This work
	Be ₃ (OH) ₃ L ²⁺	-7.56 ± 0.04	This work
Lactic acid	BeL ⁺	1.30 ± 0.15	This work
	Be ₃ (OH) ₃ L ²⁺	-7.03 ± 0.09	This work
	BeL ⁺	0.40	21 ^a
2-Hydroxyisobutyric acid	BeL ⁺	1.15 ± 0.04	This work
	BeL ₂	3.04 ± 0.03	This work
	Be ₃ (OH) ₃ L ²⁺	-7.22 ± 0.12	This work
	BeL ⁺	1.16	13
	BeL ₂	2.65	13
	BeH ₋₁ L	-3.68	13
	Be ₃ (OH) ₃ L ₃	-4.68	13

^a 1.0 M NaClO₄.

Table 4. Stability constants [log(β ± 3σ)] of beryllium(II) complexes of (+)-tartaric acid (0.5 M NaClO₄, 25 °C).

Formula	This work	Ref. 14	Ref. 22 ^a
BeL	1.52 ± 0.01	1.69	1.74
BeL ₂ ²⁻	3.20 ± 0.06	2.93	
BeH ₋₁ L ⁻			-2.66
Be(H ₋₁ L) ₂ ⁴⁻	-6.12 ± 0.16	-6.52	
Be ₂ H ₋₂ L ₂ ²⁻			-1.46
Be ₃ (OH) ₃ L ⁺	-5.56 ± 0.12	-5.49	
Be ₃ (OH) ₃ (H ₋₁ L)	-10.86 ± 0.14	-10.49	
Be ₄ H ₋₆ L ₂ ²⁻			-15.27
Be ₄ H ₋₆ L ₄ ⁶⁻			-9.83

^a 1.0 M KNO₃.

-3.20 and log β_{-2,1,0} = -11.0.⁵ The protonation constants of the ligands were reported recently, and are presented in Table 2.¹⁶

Results and discussion

Glycolic, lactic and 2-hydroxyisobutyric acids. At pH 6.2–6.3 a white precipitate was formed in all of these beryllium–ligand acid systems. Therefore, only the data collected before this pH were used to calculate the equilibrium models and stability constants. The curves representing Z_{A/C} vs. -log h and \bar{n} vs. log[L] indicated the formation of only weak mononuclear BeL_n complexes at pH < 3.5. For glycolic and 2-hydroxyisobutyric acids the data were described by the formation of two complexes, namely BeL⁺ and BeL₂. The following stability constants were obtained: log β_{0,1,1} = 1.05 ± 0.02 and log β_{0,1,2} = 2.85 ± 0.01 for glycolic acid, and

Table 5. Stability constants [log(β ± 3σ)] of beryllium(II) complexes of citric acid (0.5 M NaClO₄, 25 °C).

Formula	This work	Ref. 15 ^a	Ref. 23 ^b
BeL ⁻	4.40 ± 0.03	4.31 ± 0.03	4.5
BeL ₂ ⁴⁻	8.12 ± 0.20		
Be ₂ L ₂ ²⁻	12.77 ± 0.06	13.10 ± 0.01	
BeHL	7.36 ± 0.07	7.56 ± 0.07	2.2 (log K)
BeH ₂ L ⁺			1.4 (log K)
Be ₂ H ₋₁ L ₂ ³⁻		8.23 ± 0.01	
Be ₂ H ₋₂ L ₂ ⁴⁻	2.98 ± 0.13	3.15 ± 0.02	
Be ₂ H ₋₃ L ₂ ⁵⁻	-4.12 ± 0.22		
Be ₄ H ₋₂ L ₂		10.78 ± 0.06	
Be ₄ H ₋₃ L ₂ ⁻		7.08 ± 0.04	
Be ₄ H ₋₄ L ₂ ²⁻		1.97 ± 0.08	

^a 1.0 M KNO₃, 25 °C. ^b 0.15 M, 34 °C.

log β_{0,1,1} = 1.15 ± 0.04 and log β_{0,1,2} = 3.04 ± 0.03 for 2-hydroxyisobutyric acid [the errors given correspond to 3σ(log β_{p,q,r})]. The values for the BeL₂ complexes are slightly higher than were expected on the grounds of the studies of Duc and Thomas-David (Table 3).¹³ The high stability constants for the BeL₂ complexes compared to the BeL⁺ complexes indicate that these complexes form nearly simultaneously. The same property was also found for tartaric acid discussed later in this paper. For lactic acid only the BeL⁺ species was detected in this pH region, giving the stability constant log β_{0,1,1} = 1.30 ± 0.15. In this case beryllium acts like copper, which was studied in our earlier work.¹⁷ According to the investigations of Tedesco and DeRumi²¹ this complex would be considerably weaker than the stability determined in our work indicated. They compared the stabilit-

ies of propionate and lactate complexes with three metals (Be^{2+} , Al^{3+} and Cr^{3+}) and reported the stability constants only for the ML complexes.

According to the $Z_{A/C}$ vs. $-\log h$ curves it was evident that hydrolyzed complexes were formed at $\text{pH} > 3.5$. The stoichiometry of this or these species were determined by testing different p,q,r combinations and selecting the model giving the lowest value of U . As is known from the hydrolysis studies of beryllium, the main species in which beryllium exists in aqueous solution is the trimer $\text{Be}_3(\text{OH})_3^{3+}$. Thus, it is obvious that this species forms complexes with the ligands studied. The best fit was obtained with $\text{Be}_3(\text{OH})_3\text{L}^{2+}$ instead of the $\text{Be}_3(\text{OH})_3\text{L}_3$ species proposed in the earlier work.¹³ Also the deprotonated complex BeH_{-1}L (the proton from the α -OH group of the ligand acid is dissociated) was tested with and without other complexes, but the U -value was not lowered, and thus the model was no better with this species. The same model was found to fit for all the monocarboxylic acids studied giving the following stability constants: $\log \beta_{-3,3,1} = -7.56 \pm 0.04$, $\log \beta_{-3,3,1} = -7.03 \pm 0.09$ and $\log \beta_{-3,3,1} = -7.22 \pm 0.12$

for glycolic, lactic and 2-hydroxyisobutyric acid, respectively.

The calculated $Z_{A/C}$ vs. $-\log h$ curves indicated the correctness of our model for these systems, from which the one for 2-hydroxyisobutyric acid is presented as an example (Fig. 1a). The distribution diagrams for systems of beryllium(II) with glycolic, lactic and 2-hydroxyisobutyric acids are presented in Figs. 2a–2c. These diagrams show that the complex formation of beryllium (II) with these ligands is considerably weak, and hence, the main species remains as $\text{Be}_3(\text{OH})_3^{3+}$.

Tartaric acid. At $\text{pH} < 3.5$ the beryllium(II)–tartaric acid system is described by the formation of the binary mononuclear complexes BeL and BeL_2^{2-} . The graphical representations of the experimental data showed clearly that protonated or polynuclear complexes were not formed in this pH region. The following stability constants were obtained in this work: $\log \beta_{0,1,1} = 1.52 \pm 0.01$ and $\log \beta_{0,1,2} = 3.20 \pm 0.06$. The stability of the BeL_2^{2-} species is considerably higher when compared to the results obtained by Duc and Thomas-David (Table 4).¹⁴

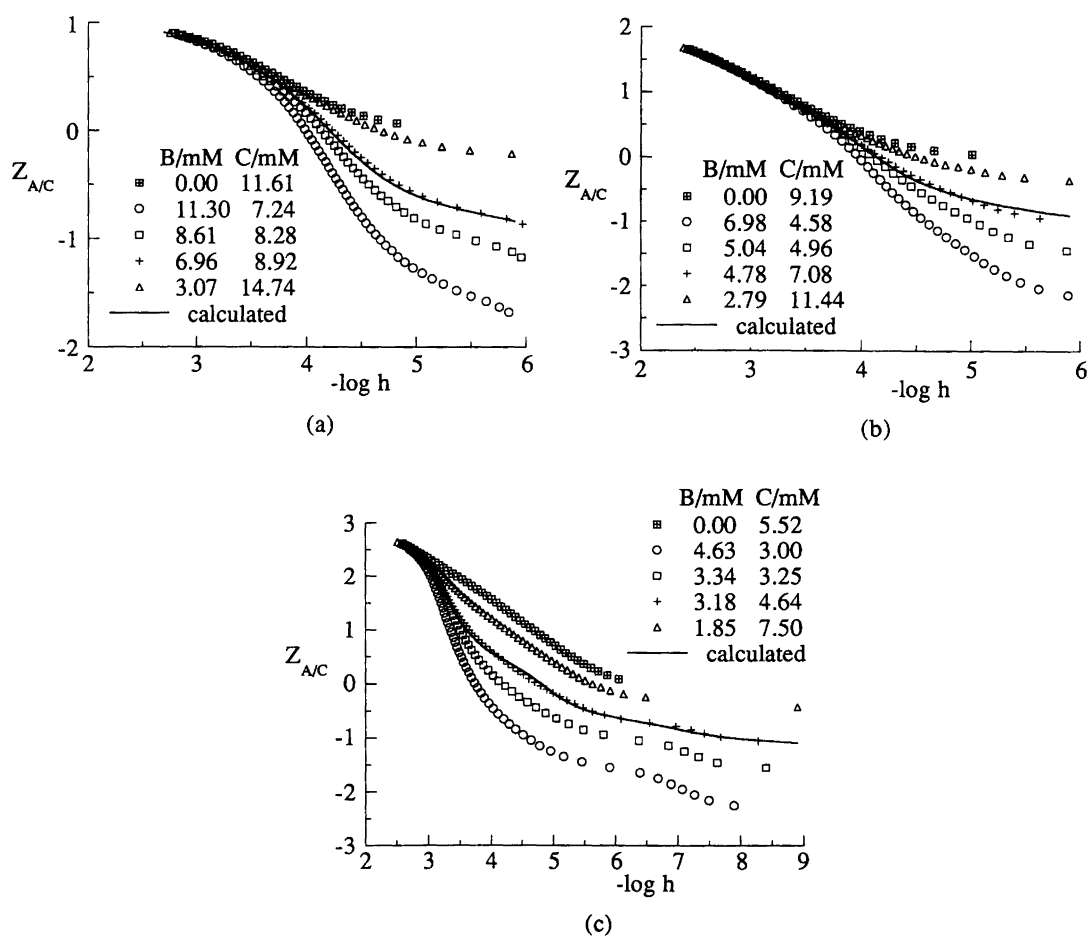


Fig. 1. Experimental data for beryllium(II)-ligand acid, viz. 2-hydroxyisobutyric (a), L(+)-tartaric (b) and citric (c), systems plotted as $Z_{A/C}$ vs. $-\log h$. The concentrations of beryllium (B) and ligand (C) in separate titrations are given in the figure. The full curves have been calculated with the stability constants determined in this work.

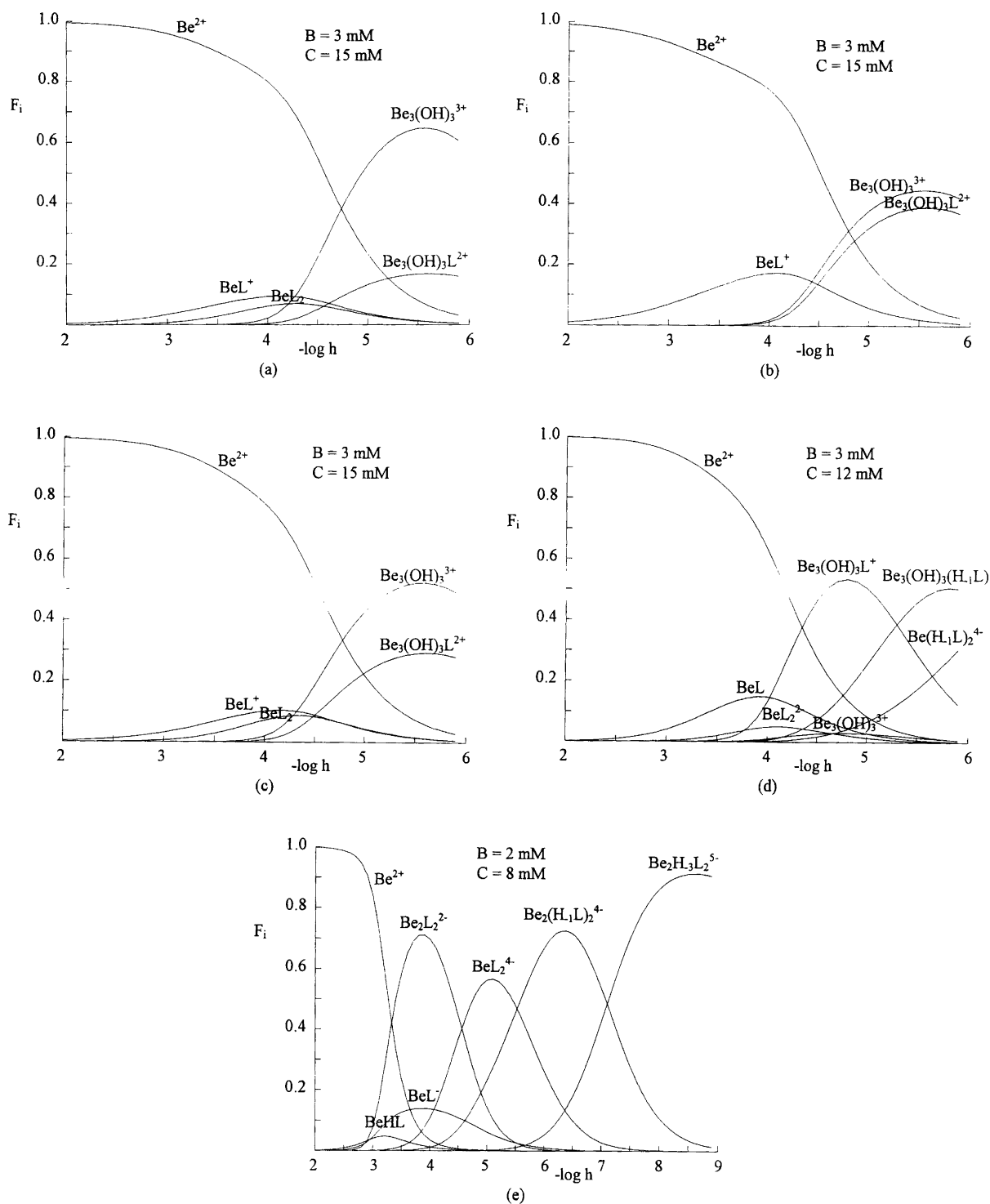


Fig. 2. Distribution diagrams F_i [fraction of total beryllium(II)] vs. $-\log h$ for beryllium(II)-ligand acid, viz. glycolic (a), lactic (b), 2-hydroxyisobutyric (c), L(+)-tartaric (d) and citric (e), systems (B =beryllium concentration and C =ligand concentration). The calculations have been made using the program SOLGASWATER with constants determined in this work (Tables 3-5).

The pH range of the titrations was restricted to $\text{pH} < 6.3$ by the precipitation of white product. At the $\text{pH} 3.5$ the formation of hydrolyzed complexes begins. Up to $\text{pH} 5$ the main species was found to be $\text{Be}_3(\text{OH})_3\text{L}^+$, which was also obtained for the monocarboxylic acids discussed earlier. Thereafter, it is assumed

that the proton from the α -OH group of the ligand dissociates, resulting in $\text{Be}_3(\text{OH})_3(\text{H}_{-1}\text{L})$. Also, a species with a p,q,r triplet $-2,1,2$ was found to form, which is probably due to the hydrolyzation of the BeL_2^{2-} complex to form minor species $\text{Be}(\text{H}_{-1}\text{L})_2^{4-}$. Several other complexes were tested in the search of the complex model,

including the species found by other workers, but a better fit was not obtained. Thus, the complexes found in this work are identical to the complexes found by Duc and Thomas-David,¹⁴ whereas the complex model proposed by Vanni *et al.*²² differs considerably from our results. The stability constants calculated for the complexes mentioned above are as follows: $\log \beta_{-3,3,1} = -5.56 \pm 0.12$, $\log \beta_{-4,3,1} = -10.86 \pm 0.14$ and $\log \beta_{-2,1,2} = -6.12 \pm 0.16$.

The calculated $Z_{A/C}$ vs. $-\log h$ curve deviates slightly from the corresponding experimental curve at $\text{pH} > 5$, which can be caused by some uncertainty in the determined stability constants. The distribution diagram for the beryllium(II)–tartaric acid system shows that the amount of $\text{Be}_3(\text{OH})_3^{3+}$ is very small, and thus most of the beryllium is in a complexed form at $\text{pH} > 5$ (Fig. 2d).

Citric acid. The titrations for beryllium(II)–citric acid system were not restricted by any precipitation at the $\text{pH} < 9$. In contrast to the tartaric acid system discussed earlier citric acid forms very stable complexes already at low pH . \bar{n} ($\log[\text{L}]$) curves were plotted in order to indicate the possible formation of protonated or polynuclear complexes (Fig. 3). If only mononuclear binary complexes are formed, the curves will coincide regardless of concentrations B and C . The different concentration ratios C/B gave clearly different curves, and therefore the protonated and polynuclear complexes had to be tested. The experimental data below $\text{pH} 4$ were best described by the formation of three complexes, namely BeL^- , BeHL and $\text{Be}_2\text{L}_2^{2-}$, with the following stability constants: $\log \beta_{0,1,1} = 4.40 \pm 0.03$, $\log \beta_{1,1,1} = 7.36 \pm 0.07$ and $\log \beta_{0,2,2} = 12.77 \pm 0.06$. These constants are in good agreement with the values determined earlier, and the equilibrium model for this pH range proposed by Vanni and Gennaro is confirmed (Table 5).^{15,23}

According to our studies the formation of hydrolyzed complexes begins at $\text{pH} 4$. The main species at the neutral pH region was found to have the p,q,r combination $-2,2,2$. This combination is best explained by the forma-

tion of the complex, where the $\text{Be}_2\text{L}_2^{2-}$ species is hydrolyzed to result $\text{Be}_2(\text{H}_{-1}\text{L})_2^{4-}$. Also the mononuclear BeL_2^{4-} complex was found to form, and it was calculated together with the hydrolyzed complexes. Several other p,q,r combinations were tested in order to get a better fit in the LETAGROP calculations. The $Z_{A/B}$ (the average number of protons per each metal atom) approached in each titration the value -1.5 , indicating the formation of complexes with the ratio of $\text{Be}:\text{H}$ equal to $1:-1.5$. The calculations gave the lowest U -value for the species having the stoichiometric relation $\text{Be}:\text{H}:\text{L}$ equal to $2:-3:2$. Also the dimer and trimer of this species were tested, but the best fit was obtained with the complex $\text{Be}_2\text{H}_{-3}\text{L}_2^{5-}$. Owing to the fact that citric acid has only one α -OH group to be deprotonated it is obvious that this complex must be a mixed hydroxo complex. An answer to the question how many hydroxo groups the species contains cannot be given from present data. Therefore, the complex is presented in the form written above. The following stability constants were obtained in the calculations: $\log \beta_{0,1,2} = 8.12 \pm 0.20$, $\log \beta_{-2,2,2} = 2.98 \pm 0.13$ and $\log \beta_{-3,2,2} = -4.12 \pm 0.22$.

The stability constant for the $\text{Be}_2(\text{H}_{-1}\text{L})_2^{4-}$ complex is in good accord with the constant determined earlier, whereas the composition of the other complexes in this pH region differ totally from the equilibrium model determined by Vanni and Gennaro.¹⁵ The polynuclear complexes they reported, viz. $\text{Be}_4\text{H}_{-2}\text{L}_2^-$, $\text{Be}_4\text{H}_{-3}\text{L}_2^-$ and $\text{Be}_4\text{H}_{-4}\text{L}_2^{2-}$, were also considered in our work, but they did not describe our experimental data. The equilibrium model determined in this work was tested by calculating the $Z_{A/C}$ values using the stability constants mentioned above and concentrations of metal and ligand that were the same as those in one of the experimental curves. The curve obtained from the SOLGASWATER calculations indicated clearly the correctness of the model (Fig. 1c). The distribution diagram for the beryllium(II)–citric acid system is presented in Fig. 2e. The diagram shows that beryllium is totally complexed at $\text{pH} 4.5$.

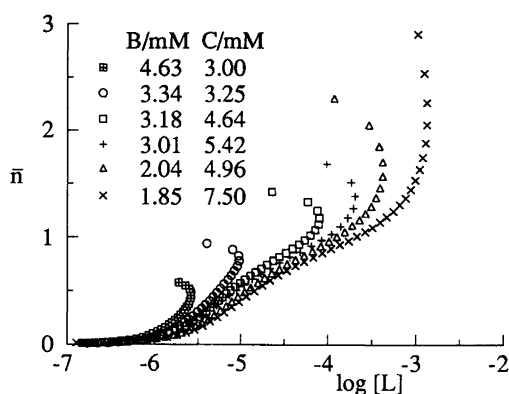


Fig. 3. Experimental data for beryllium(II)-citric acid system plotted as \bar{n} ($\log[\text{L}]$) curves. The concentrations of beryllium (B) and citric acid (C) in separate titrations are given in the figure.

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