Complexation of Benzoate Ligand With the Divalent d^{10} Acceptors at Different Temperatures

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The complex formation between zinc(II), cadmium(II), mercury(II) and benzoate ions was studied potentiometrically with glass electrode at different temperatures. The measurements have been performed in a perchlorate medium of the unit ionic strength at 25, 30, 35 and 40°C.

The stability constants of the complexes were found in the order of increasing softness i.e. Zn(II) < Cd(II) << Hg(II).

Key words: benzoate complexes; zinc compound; cadmium compound; mercury compound; thermoydnamics.

Introduction

Of the oxygen donor ligands, the simplest aromatic monocarboxylate, i.e. benzoate, ion has special interest in complexation behaviour as it forms weak complexes with most metal ions in aqueous solution[1,2]. For most of the metal-benzoate complexes, the competitions from the water molecules are profound, thus reflecting on the values of thermodynamic functions. Donors of the strong tendency to the acceptors can indeed compete most effectively with the solvent molecules forming strong complexes in either large negative values of entalphy changes or highly positive entropy changes, but not both. Metal ions-benzoate interactions have been interpreted as mainly electrostatic[2,3]. For this kind of interaction, the large amount of energy required to break the metal-ion water and ligand-water bonds is, in most cases, not compensated by the formation of the new metal-benzoate bonds. Consequently, the net reaction tends to be more endothermic or less exothermic. Furthermore, breaking the hydrate structures into a less ordered or more probable state by complex formation will cause a large gain of entropy, which thus becomes the driving force of the metal-benzoate complex reaction[3,4]. As the complex formation proceeds, the hydration of the central ion decreases for each consecutive step and also does the entropy changes. On the other hand, the reaction tends simultaneously to be less endothermic.

The potentiometric titrations were utilized to study the complexation of the benzoate ion with Zn(II), Cd(II) and Hg(II) in an aqueous solution of unit ionic strength with NaClO$_4$ as supporting electrolyte at 25,

30, 35 and 40°C, providing temperature dependent constants and thus, enthalpies and entropies. Here, the free benzoate ion concentration [L] was determined via pH measurements in metal ion solutions containing benzoate-benzoic acid buffers. This technique can be used for many ligands which are anions of weak acids.

Stability data referring to the benzoate ligand already exist in the case of Zn(II) and Cd(II). For Hg(II), such data were determined in the present study.
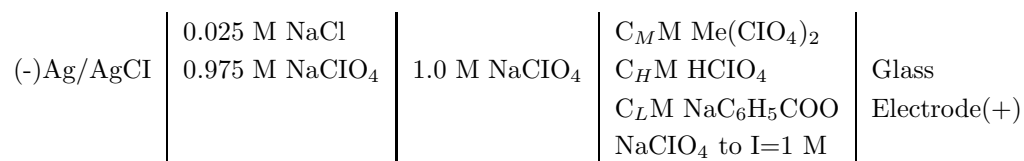
Experimental

Chemicals

The preparation, purification and standardization of zinc(II), cadmium(II), mercury(II)-perchlorates and sodium perchlorate were carried out as described previously[5,6]. Sodium benzoate solutions were made from C_6H_5COONa (Bayer). The Ag/AgCl electrodes were prepared as reported elsewhere[1,2,5].

Measurements

A Metrohm 654 pH meter was used for the potentiometric measurements. The glass electrode was a Metrohm EA 109 with a slope of 59.2±0.2 mV at 25°C.

The procedure and the measurement technique have been described elsewhere[1,2,5]. The emfs of the following cell were measured.

(-)Ag/AgCI	0.025 M NaCl 0.975 M NaCIO$_4$	1.0 M NaCIO$_4$	C$_M$M Me(ClO$_4$)$_2$ C$_H$M HClO$_4$ C$_L$M NaC$_6$H$_5$COO NaClO$_4$ to I=1 M	Glass Electrode(+)

where Me denotes Zn(II), Cd(II) or Hg(II). Measurements were done as titrations at a constant metal ion concentration, C$_M$, and constant acid concentration, C$_H$. Here, the free hydrogen ion concentration [H$^+$] is measured in buffer containing metal ions. The free ligand concentration [L] of the complex solution and the corresponding values of the ligand number $\bar{n}$ can be found if the acidity constant of benzoic acid is known under the prevailing condition. The values of acidity constants of benzoic acid at different temperatures have been determined earlier [1]. Once corresponding values of $\bar{n}$ and [L] are obtained, the formation constants can be evaluated from a graphical integration of $\bar{n}/[L]$ vs. [L] plot[1,2,6].

Results and Discussion

Zn(II)-benzoate system

Measurements have been carried out with the values of C$_M$ ranging from about 30 to 70 mM with C$_M$/C$_H$ ratios as 2.2, 3.4, 3.8 and 4.7. Thus, it was possible to check the formation of polynuclear or/and hydrolytic complexes (if any). No systematic trends were observed among the series used except C$_M$ >50 mM, due to changes in the activity coefficients. A free ligand concentration up to 80 mM was reached in the titrations. The $\bar{n}/[L]$ vs [L] plot is the same for each C$_M$ and C$_H$ value showing that only the mononuclear first complex forms in an appreciable amount. The graphical and numerical evaluations of the formation constants at 30, 35 and 40°C indicate the formation of the first complex. However, at 25 °C, the formation of the second

mononuclear complex also takes place in the range of ligand concentration used. The following over-all stability constants are found for Zn(II)-benzoate system at 25 °C

$$\beta_1 = 6.1 \pm 0.3 M^{-1}$$
$$\beta_2 = 12 \pm 4 M^{-2}$$

The errors correspond to graphical estimated uncertainties. The value of β_1 is almost the same at 30, 35 and 40 °C, i.e., it does not change appreciably, which implies $\Delta H_1^\circ \cong 0$.

Cd(II)-benzoate system

The potentiometric titrations were performed with five different values of C_M ranging between 20-35 mM with C_M/C_H ratios varying from 1.9 to 5.4. No systematic deviations were observed between the series used. Thus, neither polynuclear nor acid complexes seems to form in the concentration range at the temperatures measured.

The following equilibria data were found:

t/°C	β_1/M^{-1}	β_2/M^{-2}
25.0	12.7±0.3	39±3
30.0	12.7±0.3	28±3
35.0	12.4±0.3	24±4
40.0	12.4±0.4	22±6

The errors given are the estimated errors from the graphical calculations. From the dependence of the formation constants upon the temperatures, with the assumption that both the enthalpy and entropy changes are constant in the ranges of the temperature applied, a rough value of ΔH_j° and ΔS_j° were obtained by the equation $\ln \beta_j = -\frac{\Delta H_j^\circ}{RT} + \frac{\Delta S_j^\circ}{R}$. However, such estimations of both ΔH° and ΔS° can always give very unreliable results when weak complex formations take place. A direct calorimetric measurement will give very precise values for ΔH° and ΔS°.

Hg(II)-benzoate system

Contrary to Zn^{2+} and Cd^{2+}, Hg^{2+} forms stronger complexes with benzoate ligands. Since stronger complexes form in this system, low metal ion concentrations can be used. Titrations were carried out with C_M varying between 0.4 and 0.7 mM. Precipitation of white Hg(C$_6$H$_5$COO)$_2$ takes place at higher metal ion concentrations. The highest free ligand concentration attained in the titration was 1.7 mM. As Hg^{2+} hydrolysis occurs at higher pH values, titration was performed with benzoic acid-benzoate buffers at around pH=pK. The formation constants were evaluated graphically by plotting $\bar{n}/[L]$ vs. $[L]$ plot[7]. The complex formation function is independent of both C_M and C_H, which indicates the formation of only mononuclear complexes. The following results were obtained for Hg^{2+}-benzoate complexes at different temperatures:

t/°C	β_1/M^{-1}	β_2/M^{-2}
25.0	(7.0±0.5)10^3	(1.4±0.3)10^7
30.0	(6.8±0.5)10^3	(9.0±0.4)10^6
35.0	(6.6±0.6)10^3	(8.0±0.4)10^6
40.0	(6.5±0.6)10^3	(6.0±0.6)10^6

Here again, the errors given correspond to the estimated errors from the graphical calculations.

The overall stability constants β_j calculated for the benzoate complexes of the divalent d^{10} acceptors at different temperatures are listed in Table 1.

Table 1. Overall formation constants β_j for the formation of zinc(II), cadmium(II) and mercury(II)-benzoate systems at different temperatures and I=1M.

	t/°C	25	30	35	40
SYSTEM	j	β_j/M^{-j}			
Zn(II)-benzoate	1	6.1±0.3	6.1±0.3	6.1±0.3	6.1±0.3
	2	12±4			
Cd(II)-benzoate	1	12.7±0.3	12.7±0.3	12.4±0.3	12.4±0.3
	2	39±3	28±3	24±3	22±6
Hg(II)-benzoate	1	(7.0±0.5)10^3	(6.8±0.5)10^3	(6.6±0.6)10^3	(6.5±0.6)10^3
	2	(1.4±0.3)10^7	(9.0±0.4)10^6	(8.0±0.4)10^6	(6.0±0.6)10^6

The benzoate ligands do not form complexes in appreciable amounts with Zn^{2+} up to concentrations of [L]$\cong$80 mM. Certainly, very weak complexes are formed with benzoate ligands. At temperatures over 25 °C, the formation of the second mononuclear complex does not take place in a measurable quantity. No reliable enthalpy and entropy values can be obtained from the temperature-dependent stability constants for the zinc-benzoate system. Potentiometric measurements at 25, 30, 35 and 40 °C give almost the same value of β_1 within the experimental errors. This implies that $\Delta H_1^\circ \cong 0$, and there is a ΔS_1° value of about 15 J.mol^{-1}.K^{-1} for this system.

For cadmium, the results show that the benzoate ligand forms two well-defined mononuclear complexes in the concentration range studied. The variation of $\ln\beta_1$ with 1/T gives a value of $\Delta H_1^\circ \cong$-1.5 kJ.mol^{-1} and $\Delta S_1^\circ \cong$ 16 J.mol^{-1}.K^{-1}. The same estimations for the second complex give, for the over-all values, $\Delta H_{II}^\circ \cong$-30 kJ.mol^{-1}. $\Delta S_{II}^\circ \cong$-70 J.mol^{-1}:K^{-1}.

Zinc and cadmium complexes formed by the benzoate ligand are very weak. In contrast to Zn^{2+} and Cd^{2+}, much stronger complexes of Hg^{2+} are formed. The plot of $\ln\beta_j$ against 1/T is quite linear for this system. As for Hg^{2+}, slightly more exothermic values are found for the overall enthalpy changes, i.e. ΔH_1°=-3.9±0.6 and ΔH_{II}°=-41±11 kJ.mol^{-1}. The entropy changes are highly positive, ΔS_1°=60±2 J.mol^{-1}.K^{-1}, for the first step. Here, $\cong$80% contribution to the stability comes from the entropy increase. On the other hand, the second step is enthalpy driven while the entropy change counteracts the complex formation.

The donor ability of a coordinating atom in a polyatomic ligand depends much on its neighboring structure. The character and the strength of the bonds to adjacent atoms plays on important role o the coordination of the donor atom. Furthermore, the nature of the groups adjacent to the donor atom exhibit profound steric hindrance to complexation. The stronger donor properties of aliphatic relative to aromatic derivatives is known qualitatively. For carboxylic acids, a fair amount of quantitative data in aqueous solution show the considerably lower stabilities for aromatic carboxlylates relative to corresponding aliphatic one. This increase of stability between aromatic and aliphatic complexes occurs in other solvents as well as in aqueous solutions. The difference in stability per aromatic ring seems to be somewhat smaller than in aqueous solution[8].

Among the acceptors of the divalent ions of electron configuration d^{10} viz. Zn(II), Cd(II) and Hg(II), the hardness decreases from the fairly hard zinc to the intermediate cadmium and to the very soft mercury ion. Along this series, the covalency increases and the tendency for ionic bond formation decreases. Thus, stronger complexes of mercury(II) with the benzoate ion form in aqueous solution.

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