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Thermodynamics of benzoate complexes of cobalt(II), nickel(II) and manganese(II) in aqueous solution

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Abstract

The thermodynamic functions for the formation of benzoate complexes of cobalt(II), nickel(II) and manganese(II) have been determined by measuring the pertinent stability constants potentiometrically at temperatures within the range 25–40 ° C. From the enthalpy changes evaluated, and the free energy changes calculated from the stability constants, the entropy changes were found. All data refer to a sodium perchlorate medium of ionic strength 1.0 M.

INTRODUCTION

The complex formation of benzoate anion has been subject to several investigations with various cations [1–5]. Results of many of these studies, especially those pertaining to the thermodynamics of ionization of aqueous benzoic acid, are in poor agreement with each other. On the other hand, equilibrium data available for Co^{2+}, Ni^{2+} and Mn^{2+} systems are rather sparse. All of these studies have been carried out under different conditions, whereas results obtained under identical conditions are of great importance for a reliable comparison. Further studies on the formation of benzoate complexes by different techniques are necessary in a wider range of experimental conditions in order to arrive at a complete knowledge of the pertinent thermodynamic quantities. No determination of the thermodynamics of complexes formed in the cobalt(II)–, nickel(II)– and manganese(II)–benzoate systems seems to have been performed so far.

In order to determine the thermodynamic functions $\Delta G_i^{\ominus}$, $\Delta H_i^{\ominus}$ and $\Delta S_i^{\ominus}$, it is necessary either to measure the stability constants as a function of temperature or to find the enthalpy changes by direct calorimetry. Here, the determination of stability constants was made potentiometrically at 25.0,

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TABLE 1

Literature values of log β_1 for the formation of benzoate complexes

Cation	Ref. 1 (25 °C, $I = 0.1$ M)	Ref. 2 (30 °C, $I = 0.4$ M) [a]	Ref. 4 (25 °C, $I = 1$ M)	Ref. 5 (25 °C, $I \rightarrow 0$)
H^+	4.01	3.97	4.029	–
Mn^{2+}	–	–	–	2.06
Co^{2+}	–	0.55	–	1.69
Ni^{2+}	0.9	0.55	–	1.86
Zn^{2+}	0.9	0.74	–	1.70
Cd^{2+}	1.4	1.15	2.011	–
Cu^{2+}	1.6	1.51	–	–
Pb^{2+}	2.0	1.99	2.87	–

[a] $NaNO_3$ medium.

35.0 and 40.0 °C, which led to $\Delta H_i^{\ominus}$. The free energy changes $\Delta G_i^{\ominus}$ can be calculated from the stability constants β_i according to eqn. (1)

$$\Delta G_i^{\ominus} = -RT \ln \beta_i \tag{1}$$

the entropy changes $\Delta S^{\ominus}$ being found from the relationship $\Delta G_i^{\ominus} = \Delta H_i^{\ominus} - T\Delta S_i^{\ominus}$.

Previous stability results obtained by several authors for some monobenzoate complexes are collected in Table 1.

EXPERIMENTAL

Chemicals

The preparation, purification and standardization of cobalt(II) perchlorate, nickel(II) perchlorate, manganese(II) perchlorate and sodium perchlorate were carried out as described previously [6–8]. Sodium benzoate solutions were prepared from C_6H_5COONa (Bayer). The Ag/AgCl electrodes were also prepared as reported elsewhere [6–8].

Measurements

A Metrohm 654 pH meter was used for the e.m.f. measurements. The response slope of the glass electrode (Metrohm EA 109) had the theoretical value in the pH region used. A magnetic stirrer was used during the titrations. Stable e.m.f. values were obtained within a few minutes. All titrations were carried out at least four times with a reproducibility within 0.4 mV.

Measurements at $I = 1.0$ M and 25.0, 35.0 and 40 °C were performed as titrations with constant metal ion and acid concentrations, C_M and C_H, respectively. Equal but increasing volumes of solutions T_1 and T_2 were added from piston burettes to V_0 cm^3 of solutions S. Solution T_1 contained sodium benzoate and sodium perchlorate for $I = 1$ M, while S and T_2 had the compositions given below.

S: C_M M $Me(ClO_4)_2$, C_H M $HClO_4$, (1–3 C_M) M $NaClO_4$

T_2: $2C_M$ M $Me(ClO_4)_2$, $2C_H$ M $HClO_4$, (1–6 C_M) M $NaClO_4$

where Me denotes Co, Ni or Mn. As can been seen, the ionic strengths of solutions S and T_2 are higher than 1 M. When mixing the solutions during the titration, practically all the free acid in the reaction vessel will be converted into benzoic acid. The ionic strength of the resulting solution will then be 1 M.

The e.m.f. of the following cell was measured

$$\ominus\ \mathrm{Ag/AgCl}\left|\begin{array}{l}0.25\ \mathrm{M\ NaCl}\\ \\ \\ 0.975\ \mathrm{M\ NaClO_4}\end{array}\right|\ 1.0\ \mathrm{M\ NaClO_4}\left|\begin{array}{l}C_M\ \mathrm{M\ Me(ClO_4)_2}\\ C_H\ \mathrm{M\ HClO_4}\\ C_L\ \mathrm{M\ C_6H_5COONa}\\ \mathrm{NaClO_4\ to}\ I = 1\mathrm{M}\end{array}\right|\ \text{glass electrode}\ \oplus$$

Owing to the low solubility of benzoic acid in water, the total hydrogen ion concentration C_H was limited to 27 mM.

The e.m.f. of the above cell can be written as

$$E_H = E_H^{\ominus} + E_j + (RT/F)\ln h \qquad (2)$$

where $E_H^{\ominus}$ is the cell constant, E_j is the liquid junction potential and h is the free hydrogen ion concentration. The liquid junction potential E_j depends on h. However, at large ligand concentrations, it was found that E_j varied with the free ligand ion concentration [L]. This might indicate that E_j is also dependent on the concentration of $NaClO_4$ across the junction. All such effects must be carefully checked and determined separately (see ref. 9).

In the calculation of the constants, the free ligand concentration [L] and the ligand number $\bar{n}$ were obtained from eqns. (3) and (4) respectively.

$$[L] = K_a(C_H - h)/h \qquad (3)$$

$$\bar{n} = (C_L - C_H + h - [L])/C_M \qquad (4)$$

where h can be measured according to eqn. (2) and K_a, the acidity constant of benzoic acid, under the prevailing condition must be determined separately. Once the corresponding values of [L] and $\bar{n}$ are known, the constants can be evaluated as described before [10]. If only the first complex is formed relationship (5) is found

$$1/\bar{n} = 1/(\beta_1[L]) + 1 \qquad (5)$$

A plot of $1/\bar{n}$ against $1/[L]$ gives a straight line with a slope equal to $1/\beta_1$.

The values of $\Delta H^{\ominus}$ were estimated from the temperature coefficients of the stability constants. This method affords very precise measurements of the stability constants in the range of temperature studied, assuming that $\Delta H^{\ominus}$ is invariant in the interval considered. We have $\Delta H_1^{\ominus}$ values estimated from the relationship

$$d \ln \beta_i/d(1/T) = -\Delta H_i^{\ominus}/R \tag{6}$$

by determining the stability constants at 25.0, 35.0 and 40.0 °C.

RESULTS AND DISCUSSION

Proton–benzoate system

The ionization constant of benzoic acid has been determined by separate titrations with solutions which are free from metal ions in the range $0.06 < z < 0.9$. Here z is the average number of hydrogen ions bound per ligand anion L. The liquid junction potential for the exchange of ClO_4^- by L was determined as three titration series with the total benzoate concentrations $C_L = 100$, 200 and 400 mM, and found to be $E_j = -13.0$ [L] mV/M at 25.0 °C. The results found at $I = 1.0$ M for the formation of the proton–benzoate complex are shown in Table 2. It can be seen that the formation constant decreases with increase in temperature.

Cobalt(II)–benzoate system

Potentiometric measurements were carried out with $C_M = 30.54$, 40.71, 51.08 and 61.26 mM. Since the stabilities of benzoate complexes are rather weak, relatively large concentrations of the central ions must be used in order to obtain an adequate estimate of $\bar{n}$ [see eqn. (4)]. Different ratios of C_M/C_H have been used for every series, namely 0.8, 1.9, 2.3 and 2.8, respectively. A free ligand concentration up to ≈ 150 mM was reached in the titrations. However, due to the changes in the liquid junction potential and/or in the activity coefficients, stable e.m.f. values were not possible beyond [L] = 70 mM. In studies with very weak complexes, it is important to have reliable measurements of the best attainable accuracy that cover the largest possible range of concentrations.

TABLE 2

The formation of the proton–benzoate complex

T (°C)	$K = 1/K_a$ (M^{-1})	pK_a
25	1.071×10^4	4.03
30	1.048×10^4	4.02
35	1.029×10^4	4.01
40	1.008×10^4	4.00

The graphical evaluation of the constants indicates the formation of only one mononuclear complex. Complex formation beyond the first step does not take place at all. For a given value of [L], $\bar{n}$ varies neither with C_M nor with the buffer used. Consequently no polynuclear or acid complexes seem to exist in the range studied.

The evaluated values of β_1 at each temperature (25, 35 and 40 °C) are 3.5 ± 0.2 M^{-1}, 4.2 ± 0.2 M^{-1} and 4.6 ± 0.3 M^{-1}, respectively. The errors given correspond to estimated errors from the graphical calculations.

Nickel–benzoate system

Titrations were performed with three different values of C_M, i.e. 45.95, 54.93 and 73.22 mM. Values of the C_M/C_H ratio were 1.9, 2.4 and 3.5, respectively. In this system also, formation of only the first complex takes place in the range of concentrations used. Further benzoate ions are not coordinated, even at fairly large benzoate ion concentrations. Series with different values of C_M and C_H showed that no polynuclear and/or acid complexes were formed. The graphical calculations of constants at 25.0, 35.0 and 40.0 °C give the values for β_1 as 4.0 ± 0.2, 4.6 ± 0.2 and 4.9 ± 0.3 M^{-1}, respectively.

Manganese(II)–benzoate system

Four titration series with $C_M = 15.01$, 15.77, 19.11 and 22.09 mM were applied for this system. Ratios of C_M/C_H were varied from 0.60 to 0.90. The highest concentration of free ligand attained for this system was 40 mM. One mononuclear complex is formed within the range of concentrations in an appreciable amount. No systematic deviations can be observed between the different series of titrations applied. Graphical calculations of constants give $\beta_1 = 4.2 \pm 0.3$, 4.9 ± 0.4 and 5.3 ± 0.3 M^{-1} at 25, 35 and 40 °C respectively.

According to eqn. (6), plots of ln β_1 vs. $1/T$ for the three systems studied give straight lines with slopes equal to $-\Delta H_i^\ominus/R$ values.

The results of this study are collected in Table 3.

The benzoate ion is the simplest of the aromatic carboxylate ions and forms particularly weak complexes with most transition metal ions in aqueous media. As an O donor, the competition from the water molecules seems to be very strong for metal–benzoate complexes. The stability constants given in Tables 1 and 3 are, on the whole, in reasonable agreement, although the experimental conditions differ. The equilibrium data indicate that the stabilities of the divalent metal complexes studied follow the order $Co^{2+} < Ni^{2+} < Mn^{2+}$. The position of Mn^{2+} is especially interesting for the benzoate ligand. Generally, for numerous O and N donors, the stabilities follow the Irving–Williams order $Zn^{2+} < Cu^{2+} > Ni^{2+} > Co^{2+} > Fe^{2+} >$

TABLE 3

Overall formation constants and values of $\Delta G_1^{\ominus}$, $\Delta H_1^{\ominus}$ and $\Delta S_1^{\ominus}$ for the formation of the Co(II)-, Ni(II)- and Mn(II)-benzoate systems at 25.0 °C and $I = 1.0$ M; errors given correspond to estimated errors

System	β_1 (M^{-1})	$-\Delta G_1^{\ominus}$ (kJ mol^{-1})	$\Delta H_1^{\ominus}$ (kJ mol^{-1})	$\Delta S_1^{\ominus}$ (J mol^{-1} K^{-1})
Co(II)-benzoate	3.5 ± 0.2	3.1 ± 0.1	14.2 ± 0.8	58 ± 3
Ni(II)-benzoate	4.0 ± 0.2	3.4 ± 0.1	10.5 ± 0.7	47 ± 2
Mn(II)-benzoate	4.2 ± 0.3	3.6 ± 0.2	12.0 ± 1.0	52 ± 3

Mn^{2+}. In some cases, the order of stabilities depends upon the type of ligand as well.

Our value of K at 25.0 °C for the proton–benzoate system is in excellent agreement with $K = (1.068 \pm 0.001)$ 10^4 M^{-1} obtained by Olin and Svanström [4] under the same conditions. The value of K decreases with increase in temperature over the range 25–40 °C from 1.071×10^4 to 1.008×10^4 M^{-1}. The calorimetric study of Matsui et al. [3] over a wide range of temperatures shows that $\Delta H^{\ominus}$ for the formation of the proton–benzoate complex varies significantly with temperature [3]. Thus, at infinite dilution, the value of $\Delta H^{\ominus}$ changes from -106 cal mol^{-1} to $+455$ cal mol^{-1} when the temperature changes from 25 °C to 40 °C. A plot of ln K vs. $1/T$ is a linear curve. From the slope, a value of $\Delta H^{\ominus} \approx -3$ kJ mol^{-1} could be estimated for the proton–benzoate formation reaction, which is much more negative than the value of -106 cal mol^{-1} found by Matsui et al. at $I \to 0$. It is an open question whether this difference is due only to the difference in ionic medium or/and to the method of determination.

In highly polar solvents, such as water, the interactions between hard acceptors and donors are, at least for the first step, as a rule endothermic. The complex formation is thus due to a large positive entropy change. For the formation of a complex between a hard acceptor and a hard donor, the large amount of energy required to break the metal ion–water and ligand–water bonds is usually not compensated for by the formation of the metal–ligand bond. The net reaction thus tends to be endothermic [11].

The oxygen donors, next to the fluoride ion, are the hardest ones that exist. As an oxygen donor, benzoate ion forms very weak complexes with acceptors of medium hardness, such as cobalt(II), nickel(II) and manganese(II), in endothermic reactions. All three of these complexes are entropy stabilized, while the enthalpy term is positive and thus counteracts the complex formation.

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