ELSEVIER Thermochimica Acta 247 (1994) 407-413

The thermodynamics of benzoate complexes of copper(II) and iron(III) in aqueous solution

Betül Başaran [a], Efraim Avşar [b,*], Ayten Göçmen [a], F. Bedia Erim [a]

[a] *Department of Chemistry, Istanbul Technical University, Maslak, 80626 Istanbul, Turkey*
[b] *Department of Chemistry, Faculty of Arts and Sciences, Akdeniz University, 07070 Antalya, Turkey*

Received 9 March 1994; accepted 21 March, 1994

Abstract

The thermodynamics of the complex formation reactions of copper(II) and iron(III) with benzoate ions have been determined by measuring the formation constants at different temperatures. The benzoate complexes of fairly hard acceptors, like Fe(III), are characterized by highly positive entropy changes. All measurements were carried out potentiometrically at 25, 35 and 40°C and in an ionic medium of 1 M, with sodium perchlorate as the background electrolyte.

Keywords: Benzoate; Copper compound; Iron compound; Thermodynamics

1. Introduction

A knowledge of thermodynamics has proved useful in the systematic study of the formation of benzoate complexes of various cations in aqueous solution [1,2]. The data obtained from the measurements give valuable information about the nature of the interactions between the donors and acceptors in the complex formation reaction.

In a highly protic donor solvent, like water, the competition from solvent molecules is indeed strong for most of the metal-benzoate complexes. Ligands of strong affinity to the metal ions can compete efficiently with the solvent molecules

---

* Corresponding author.

SSDI 0040-6031(94)01815-X

forming strong complexes and can release the solvent molecules completely from the inner coordination sphere. Bonding in benzoate complexes has usually been explained in terms of electrostatic interactions.

The free energy change, calculated from the formation constant, contains an entropic term and an energetic term, according to the well-known thermodynamic relation. The energetic term, i.e. the enthalpy change, is inherently determined by the difference in the metal–ligand and metal–solvent strengths. The strength of the ligand–solvent bonds must also be considered in this respect. The entropy, however, is related to microscopic disorder, or to what is called the "probability of the state". A positive entropy change means that the final state is less ordered, or more probable, than the initial state.

In order to obtain thermodynamic parameters from the measurements, potentiometric titrations were performed with a glass electrode, providing temperature-dependent formation constants, and enthalpies and entropies. The thermodynamic functions obtained in this way provide a basis for interpretation of the complex formation reactions.

2. Experimental

2.1. Chemicals

$Cu(ClO_4)_2$ was made by treating $CuCO_3 \cdot Cu(OH)_2$ (Merck, p.a.) with $HClO_4$ (Merck, p.a.). Analysis of the Cu(II) concentration in the stock solution was carried out by electrolysis. The free acid concentrations were determined potentiometrically. The preparation and standardization of iron(III) perchlorate were carried out as described previously [3]. Sodium benzoate solutions were made from C_6H_5COONa (Bayer). The Ag,AgCl electrodes, and sodium perchlorate were prepared as reported elsewhere [1,3,4].

2.2. Measurements

Potentiometric measurements were carried out with a Metrohm 654 digital pH/mV meter equipped with a glass electrode (Metrohm EA 109), and with a slope of 59.2 ± 0.1 mV. A magnetic stirrer was used for mixing. The emfs of the following cell were measured.

$$-\mathrm{RE} \parallel C_\mathrm{M}\ \mathrm{M\ Me(ClO_4)}_v, C_\mathrm{H}\mathrm{M\ HClO_4}, C_\mathrm{L}\ \mathrm{M\ C_6H_5COONa, NaClO_4}\ \text{to}$$

$$I = 1\ \mathrm{M} \mid \text{glass electrode} +$$

where RE $\parallel$ is Ag,AgCl | 0.025 M NaCl,0.975 M $NaClO_4$ | 1.0 M $NaClO_4$ |. Here, Me denotes Cu(II) or Fe(III).

Measurements were performed as titrations at constant metal ion concentration, C_M, and constant acid concentration, C_H. Equal but increasing volumes of solutions T_1 and T_2 were added from piston burettes to V_0 | cm^3 of solution S. Solution

T_1 contained sodium benzoate and sodium perchlorate for $I = 1$ M, while S and T_2 had the compositions

$$\text{S: } C_M \text{ M Cu(ClO}_4)_2,\ C_H\text{M HClO}_4,\ (1 - 3C_M) \text{ M NaClO}_4$$

$$\text{T}_2\text{: } 2C_M \text{ M Cu(ClO}_4)_2,\ 2C_H\text{M HClO}_4,\ (1 - 6C_M) \text{ M NaClO}_4$$

for the Cu(II) system, and

$$\text{S: } C_M \text{ M Fe(ClO}_4)_3,\ C_H \text{ M HClO}_4,\ (1 - C_H - 6C_M) \text{ M NaClO}_4$$

$$\text{T}_2\text{: } 2C_M \text{ M Fe(ClO}_4)_3,\ 2C_H \text{ M HClO}_4,\ (1 - 2C_H - 12C_M) \text{ M NaClO}_4$$

for the Fe(III) system.

The free hydrogen ion concentration h can be found by measuring the emfs of the above cell from the equation

$$E_H = E_H^{\ominus} + E_j + (RT/F)\ln(h) \tag{1}$$

where $E_H^{\ominus}$ is the cell constant and E_j is the liquid junction potential. E_j depends on h. At high ligand concentrations, however, it was found that E_j varies slightly with the free ligand concentration [L]. This might indicate that E_j is also dependent on the concentration of $NaClO_4$ across the junction [1].

By knowing the values of h, the free ligand concentration [L] and the ligand number, defined as $\bar{n} = (C_L - [L])/C_M$, can be calculated from

$$[L] = K_a(C_H - h)/h \tag{2}$$

and

$$\bar{n} = (C_L - C_H + h - [L])/C_M \tag{3}$$

respectively. Once the corresponding values of [L] and $\bar{n}$ are known, the complexation constants can be evaluated [1,5]. Here, K_a is the acidity constant of benzoic acid determined in separate measurements [1].

2.3. Calculation

Owing to the high tendency of iron(III) to hydrolyse in benzoate buffers containing even a large proportion of benzoic acid, the extent of hydrolysis is sufficiently large that it must be considered in the calculation of the formation constant.

If only the first mononuclear hydroxo and mononuclear benzoate complexes are formed, the following relations can be written for metal ion, acid and ligand concentrations, respectively

$$C_M = [M] + [MOH] + [ML] \tag{4}$$

$$C_H = h + [HL] - [MOH] \tag{5}$$

$$C_L = [L] + [HL] + [ML] \tag{6}$$

Using these values in Eq. (3) and remembering the expressions for the constants, after rearrangement, we obtain

$$1/(1-\bar{n}) = 1 + K/h + \beta_1[\mathrm{L}] \tag{7}$$

where K is the equilibrium constant of the reaction

$$\mathrm{Fe}^{3+} + \mathrm{H_2O} = \mathrm{Fe(OH)}^{2+} + \mathrm{H}^+ \tag{8}$$

A plot of $[1/(1-\bar{n}) - K/h]$ against [L] should give a straight line with a slope equal to β_1.

The value of $K = 1.6 \times 10^{-3}$ at 25°C and $I = 1$ M was taken from Ref. 6. At 35 and 40°C, values of K were recalculated using $\Delta H^\ominus = 45.98$ kJ mol^{-1} [7].

The values of $\Delta H_1^\ominus$ were estimated from the temperature-dependent formation constants. Assuming that $\Delta H_1^\ominus$ is constant in the interval of the temperatures studied, the $\Delta H_1^\ominus$ value was calculated from the relationship

$$\mathrm{d}\ln\beta_1/\mathrm{d}(1/T) = -\Delta H_1^\ominus/R \tag{9}$$

Plots of ln β_1 versus $1/T$ are fairly linear.

3. Results and discussion

3.1. Copper(II)-benzoate system

Measurements were carried out with $C_\mathrm{M} = 1.444$, 1.740, 2.888, 3.479, 4.301, 4.925 and 5.701 mM. In order to avoid hydrolysis, and to check that only mononuclear complexes are formed, different ratios of $C_\mathrm{M}/C_\mathrm{H}$ were used, i.e. 0.14, 0.17, 0.23, 0.35, 0.38 and 0.57, respectively. Depending on the temperature studied, a free ligand ion concentration up to 30 mM was reached in the titrations. At higher ligand concentrations, a blue precipitate, which does not dissolve at higher ligand concentrations, is observed. Potentiometric titrations were interrupted at this point.

The graphical evaluation of the constants at 35 and 40°C indicates the formation of only the first mononuclear complex. At 25°C, however, the formation of the second also takes place to some extent. Analysis of $\bar{n}/[\mathrm{L}]$ versus [L] or $1/\bar{n}$ versus 1/[L] data, Figs. 1 and 2, provides values for the first and second complex: $\beta_1 = 58 \pm 6$ M^{-1}, $\beta_2 = 230 \pm 60$ M^{-2}. The scatter of the data around the regression curve calculated for each plot is random and consistent with the accuracy of the formation constants. The errors given correspond to estimated errors based on this scatter. The graphical calculations of the first formation constants at 25.0, 35.0 and 40.0°C gave β_1 values of 58 ± 6, 55 ± 6 and 52 ± 14 M^{-1}, respectively. The plot of ln β_1 versus $1/T$ is fairly linear with a value of $\Delta H_1^\ominus = -6 \pm 2$ kJ mol^{-1}.

3.2. Iron(III)-benzoate system

The experimental procedure used here was essentially the same as described for Cu(II). Titrations were performed with different values of C_M, i.e. 0.7180, 0.8935,

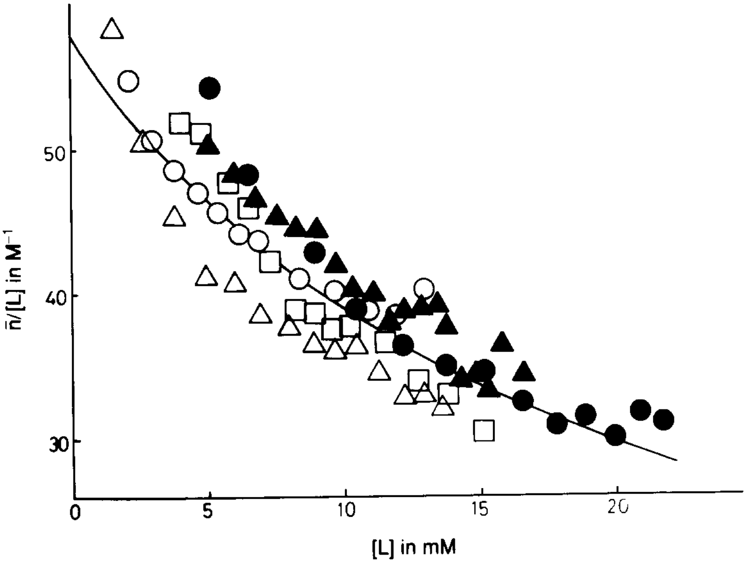

Fig. 1. The ratio $\bar{n}/[L]$ as a function of [L] for the copper(II)–benzoate system: (●) $C_M = 2.888$ mM, $C_H = 10.07$ mM; (○) $C_M = 5.701$ mM, $C_H = 15.00$ mM; (▲) $C_M = 1.444$ mM, $C_H = 10.05$ mM; (△) $C_M = 5.701$ mM, $C_H = 9.993$ mM; (□) $C_M = 4.301$ mM, $C_H = 15.00$ mM.

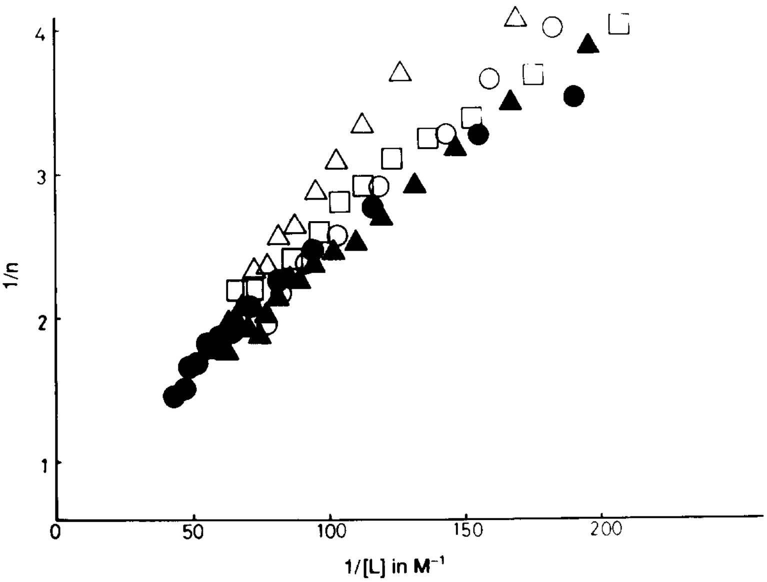

Fig. 2. The variation of $1/\bar{n}$ with $1/[L]$ for the copper(II)–benzoate system. For symbols refer to Fig. 1.

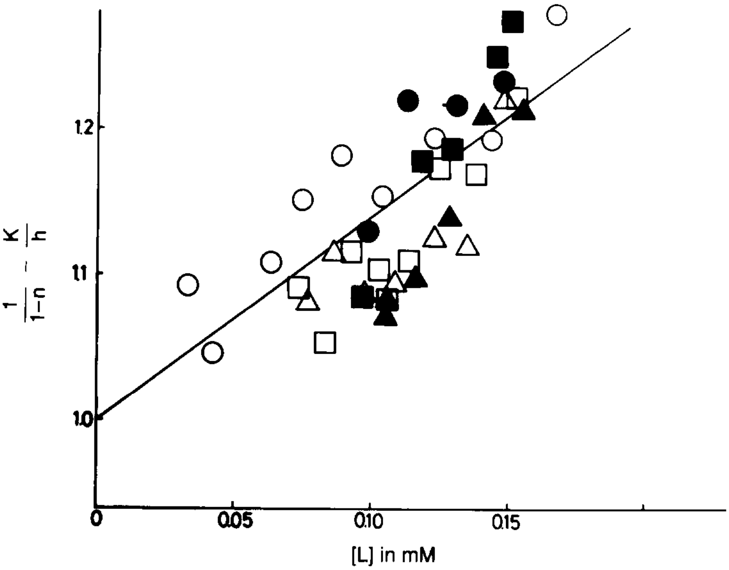

Fig. 3. The determination of β_1 for the $Fe(C_6H_5COO)^{2+}$ complex [see Eq. (7)]: (●) $C_M = 1.787$ mM, $C_H = 32.62$ mM; (○) $C_M = 0.8935$ mM, $C_H = 16.48$ mM; (▲) $C_M = 1.247$ mM; $C_H = 22.60$ mM; (△) $C_M = 0.8935$ mM, $C_H = 25.34$ mM; (■) $C_M = 1.787$ mM, $C_H = 25.18$ mM; (□) $C_M = 1.601$ mM, $C_H = 22.60$ mM.

changed between 1.64 mM and 49.29 mM. A free ligand ion concentration up to 0.26 mM could be reached. Beyond this point, together with a pH value of ≥2.5, a pink-brown precipitation is formed.

Even in benzoate buffers containing a large proportion of benzoic acid, the presence of $Fe(OH)^{2+}$ cannot be totally neglected. In order to obtain a reliable value for the benzoate complex formation, the equilibrium constant of the hydrolytic reaction for the formation of $Fe(OH)^{2+}$ should be considered.

When both C_M and C_H were changed, no systematic deviations could be observed between the different series employed. Consequently, no evidence was found for the formation of polynuclear and/or acid complexes. Analysis of potentiometric data shows that point-by-point $[1/(1-\bar{n}) - K/h]$ estimates are randomly scattered and trend-free, see Fig. 3. Only the first mononuclear iron(III)–benzoate complex, and to some extent $Fe(OH)^{2+}$, were formed in the range of concentrations studied.

The graphical calculations of β_1 (M^{-1}) give the following results: $(1.4 \pm 0.2) \times 10^3$ at 25°C, $(1.9 \pm 0.2) \times 10^3$ at 35°C, and $(2.0 \pm 0.3) \times 10^3$ at 40°C.

According to Eq. (9), the plot of $\ln \beta_1$ versus $1/T$ is a straight line with slope equal to $-\Delta H_1^{\ominus}/R$.

The results are collected in Table 1. The errors stated refer to the maximum errors estimated from the graphical evaluations.

The simplest aromatic carboxylate ion forms weak complexes with most metal ions in aqueous solution [1,2]. The competition from the water molecules is indeed strong for the benzoate ligand. Usually, the reaction of the benzoate ligand with

Table 1
Overall formation constants β_j and values of $\Delta G_j^\ominus$, $\Delta H_j^\ominus$ and $\Delta S_j^\ominus$ for the formation of the copper(II)– and iron(III)–benzoate systems at 25.0°C and $I = 1$ M

System	j	β_j in M^{-j}	$-\Delta G_j^\ominus$ in kJ mol^{-1}	$\Delta H_j^\ominus$ in kJ mol^{-1}	$\Delta S_j^\ominus$ in J mol^{-1} K^{-1}
Cu(II)–benzoate	1	58 ± 6	10.1 ± 0.3	-6 ± 2	14 ± 7
	2	230 ± 60	13.5 ± 0.7		
Fe(III)–benzoate	1	$(1.4 \pm 0.2) \times 10^3$	18.0 ± 0.4	19 ± 4	124 ± 14

hard acceptors, such as Co^{2+}, Ni^{2+}, Mn^{2+} and Fe^{3+}, is characterized by highly positive entropy changes, i.e. they are all entropy-driven reactions, which we ascribe to extensive inner sphere dehydration. The enthalpy changes are all positive and thus counteract the complex formation [1]. The large positive entropy change in the iron(III)–benzoate system evidently results from the large loss of solvating water molecules upon complexation. Large positive entropy and enthalpy changes in the formation of $Fe(C_6H_5COO)^{2+}$ complex shows that the solvent interactions are indeed significant.

For the copper(II)–benzoate system, however, the reaction is slightly exothermic. Here, ≈40% contribution to the stability comes from the entropy increase. Two mononuclear complexes are formed over the range of concentrations used at 25°C. The formation at higher temperatures of the second complex does not take place in any appreciable amount, if at all. We conclude that higher complexes beyond the first step were not present at 35 and 40°C.

The benzoate ion is an oxygen donor and should thus be considered as a rather hard ligand. In accordance with the general rule for hard–hard interactions [2,8], reactions between the benzoate ligand and fairly hard acceptors, like Fe^{3+}, Co^{2+} and Ni^{2+}, are characterized by highly positive entropy changes. The enthalpy change is generally also positive, or less negative, for this kind of interaction. The thermodynamic behaviour of hard–hard interactions is usually interpreted as mainly due to the profound changes in hydration shells accompanying the complex formation [2,8,9].

References

[1] B. Başaran, E. Avşar, F.B. Erim and A. Göçmen, Thermochim. Acta, 186 (1991) 145.
[2] E. Avşar, Doğa-Tr. J. Chem., 17 (1993) 54.
[3] E. Avşar, Acta Chem. Scand., A34 (1980) 405.
[4] E. Avşar and B. Başaran, Polyhedron, 6 (1987) 1909.
[5] F.B. Erim, E. Avşar and B. Başaran, J. Coord. Chem., 21 (1990) 209.
[6] R.M. Milburn and W.C. Vosburgh, J. Am. Chem. Soc., 77 (1955) 1352.
[7] R. Arnek and K. Schlyter, Acta Chem. Scand., 22 (1968) 1327.
[8] S. Ahrland, Struct. Bonding (Berlin), 5 (1968) 118; 15 (1973) 167.
[9] S. Ahrland, Inorg. Chem., 11 (1991) 195.