ELSEVIER Thermochimica Acta 286 (1996) 245–250

thermochimica
acta

Solubility and thermodynamic transfer functions of hexa-amminecobalt(III) and tris(ethylenediamine)-cobalt(III) hexacyanoferrates(III)

Vladislav Holba *, Renata Košická

Department of Physical Chemistry, Faculty of Science, Comenius University, 842 15 Bratislava, Slovakia

Received 15 November 1995; accepted 15 March 1996

Abstract

The solubilities of hexaamminecobalt(III) and tris(ethylenediamine) cobalt(III) hexacyanoferrates(III) were measured in water as well as in binary mixtures of water with *tert*-butyl alcohol and acetonitrile as a function of temperature. The Gibbs energies, enthalpies and entropies of transfer have been evaluated from experimental data. The contribution of $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$ and $[Fe(CN)_6]^{3-}$ ions to the Gibbs energies of transfer of the investigated salts have been calculated using the TATB reference electrolyte assumption.

Keywords: Cobalt(III) complexes; Solubility; Transfer functions

1. Introduction

Solubility measurements of sparingly soluble salts in water and in water–organic solvent mixtures can be used for the evaluation of their thermodynamic transfer functions. Hexaamminecobalt(III) and tris(ethylenediamine)cobalt(III) hexacyanoferrates(III) are thermodynamically and kinetically stable, and their solubility can be determined spectrophotometrically due to the high extinction coefficient of the hexacyanoferrate(III) ion in the visible region. The solubility of hexaamminecobalt(III) hexacyanoferrate(III) in aqueous solutions of different electrolytes are reported in Refs. [1–3], and the corresponding data for tris(ethylenediamine)-cobalt(III) hexacyanoferrate(III) in water and in water–alcohol mixed solvents are reported in Ref. [4]. However, only scarce data exist on the thermodynamic functions of transfer of these

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* Corresponding author.

PII: S0040-6031(96)02970-X

salts from water to water–organic mixed solvents. The aim of our work was to determine the solubility of $[Co(NH_3)_6][Fe(CN)_6]$ and $[Co(en)_3][Fe(CN)_6]$ (en is ethylenediamine) in water and in the mixtures of water with *tert*-butyl alcohol and acetonitrile as a function of temperature, and to evaluate the Gibbs energies, enthalpies and entropies of transfer for the investigated salts. The contributions of the ions of the salts to their Gibbs energies of transfer are also assessed.

2. Experimental

Hexaamminecobalt(III) and tris(ethylenediamine)cobalt(III) hexacyanoferrates(III) were prepared by precipitation of the saturated solutions of the corresponding chlorides with a saturated solution of potassium hexacyanoferrate(III). The purity of the prepared salts was checked by elemental analysis. *tert*-Butyl alcohol and acetonitrile (both Merck, reagent grade) were distilled prior to use. Double-distilled water was used throughout.

The solubilities were determined by stirring an excess of the complex salt with approx. 50 cm^3 of the solvent in a jacketed vessel kept at a desired temperature ($\pm 0.05°C$). The equilibrium between the solid phase and the saturated solution was achieved after 4 h of stirring. Longer equilibration gave the same result. The solubility of both investigated salts was determined by measuring the absorbance at 420 nm where $[Fe(CN)_6]^{3-}$ exhibits a maximum with the absorption coefficient 1035 mol^{-1} kg cm^{-1}. The absorption coefficients of the ions $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ at this wavelength are 12 and 30 mol^{-1} kg cm^{-1} respectively and the appropriate corrections were introduced in the calculations of concentrations of the complex salts. The measurements of the absorbance were performed using Specord UV-VIS and Specol 11 spectrophotometers (both Carl Zeiss, Jena).

3. Results and discussion

The solubility of the investigated complex salts in water, and in water–*tert*-butyl alcohol and water–acetonitrile solvents of various composition and at various temperatures are summarized in Tables 1 and 2. The solubilities in water, S^{w}, and in the solvent mixture, S^{mix}, are related to the Gibbs energy of transfer of the salt, $\Delta_{tr}G^0$ by the equation

$$\Delta_{tr}G^0 = 2\,RT\ln[S^{w}/S^{mix})(\gamma_{\pm}^{w}/\gamma_{\pm}^{mix})] \tag{1}$$

The solubilities were corrected to infinite dilution using the mean activity coefficients $\gamma\pm$ calculated from the McInnes equation [5]

$$-\log\gamma\pm = A\,z_+z_-\sqrt{I}/(1+1.5\sqrt{I}) \tag{2}$$

where A is the Debye–Hückel parameter which depends on the solvent relative permittivity and temperature, z_+z_- are the charges of the ions, and I is the ionic strength. The relative permittivities of water–organic mixtures at various temperatures were taken from Ref. [6]. The $\Delta_{tr}G^0$ values calculated for different temperatures were fitted to Eq. (3); the coefficients a, b, c were evaluated by the method of least squares

$$\Delta_{tr}G^0 = a + bT + cT\ln T \tag{3}$$

Table 1
Solubilities, $S \times 10^5$ (mol kg^{-1}) of $[Co(NH_3)_6][Fe(CN)_6]$ in water and in water–organic mixed solvents with various composition and various temperatures

Wt%	°C					
	17	25	30	35	40	45
0	2.14 ± 0.07	3.12 ± 0.03	3.70 ± 0.07	4.58 ± 0.20	5.55 ± 0.07	6.82 ± 0.08
			tert-C_4H_9OH			
10	1.36 ± 0.04	1.97 ± 0.05	2.26 ± 0.04	3.21 ± 0.11	3.70 ± 0.13	4.65 ± 0.22
20	0.97 ± 0.02	1.27 ± 0.03	1.56 ± 0.03	1.75 ± 0.07	1.95 ± 0.09	3.07 ± 0.14
30	0.63 ± 0.02	0.83 ± 0.03	0.97 ± 0.04	1.12 ± 0.03	1.56 ± 0.07	1.95 ± 0.04
40	0.54 ± 0.02	0.63 ± 0.03	0.83 ± 0.03	1.07 ± 0.04	1.22 ± 0.06	1.66 ± 0.09
			CH_3CN			
10	5.79 ± 0.08	5.99 ± 0.06	7.01 ± 0.15	7.60 ± 0.21	8.18 ± 0.12	9.35 ± 0.06
20	4.72 ± 0.14	4.97 ± 0.15	5.31 ± 0.06	5.70 ± 0.05	6.28 ± 0.07	7.74 ± 0.11
30	3.46 ± 0.10	3.55 ± 0.15	3.65 ± 0.10	3.90 ± 0.11	4.53 ± 0.05	5.60 ± 0.03
40	3.21 ± 0.05	3.26 ± 0.12	3.51 ± 0.30	3.55 ± 0.16	3.65 ± 0.15	4.58 ± 0.06

Table 2
Solubilities, $S \times 10^4$ (mol kg^{-1}), of $[Co(en)_3][Fe(CN)_6]$ in water and in water–organic mixed solvents with various composition and various temperatures

Wt%	°C					
	17	25	30	35	40	45
0	3.17 ± 0.06	4.34 ± 0.05	5.16 ± 0.05	6.32 ± 0.07	7.64 ± 0.13	9.36 ± 0.01
			tert-C_4H_9OH			
10	0.94 ± 0.12	1.95 ± 0.06	2.37 ± 0.09	2.82 ± 0.01	3.75 ± 0.06	4.93 ± 0.16
20	0.50 ± 0.06	0.83 ± 0.01	1.05 ± 0.04	1.24 ± 0.06	1.56 ± 0.05	2.00 ± 0.02
30	0.24 ± 0.06	0.45 ± 0.03	0.53 ± 0.03	0.54 ± 0.02	0.72 ± 0.04	0.96 ± 0.06
40	0.21 ± 0.04	0.24 ± 0.01	0.29 ± 0.04	0.33 ± 0.07	0.42 ± 0.09	0.44 ± 0.05
			CH_3CN			
10	7.83 ± 0.24	9.13 ± 0.10	11.8 ± 0.1	12.4 ± 0.1	15.9 ± 0.7	16.4 ± 0.2
20	9.78 ± 0.24	11.2 ± 0.4	13.9 ± 0.2	15.6 ± 0.8	18.0 ± 0.6	21.0 ± 0.6
30	8.15 ± 0.02	8.34 ± 0.11	8.70 ± 0.20	9.50 ± 0.20	10.7 ± 0.2	11.7 ± 0.3
40	4.69 ± 0.13	4.86 ± 0.03	5.02 ± 0.22	5.42 ± 0.22	6.00 ± 0.16	6.81 ± 0.12

With respect to the relations $(\mathrm{d}\Delta G/\mathrm{d}T) = -\Delta S$, and $\Delta G = \Delta H - T\Delta S$, Eq. (4) and Eq. (5) represent the enthalpy and entropy of transfer

$$\Delta_{tr}H^0 = a - cT \tag{4}$$

$$\Delta_{tr}S^0 = -b - c(1 + \ln T) \tag{5}$$

The results in Table 1 show that $[Co(en)_3][Fe(CN)_6]$ is more soluble in all investigated media than $[Co(NH_3)_6][Fe(CN)_6]$. At the same time, both complex salts are more soluble in water than in water–*tert*-butyl alcohol mixtures, the solubility of $[Co(NH_3)_6][Fe(CN)_6]$ in the mixtures with lower concentrations of acetonitrile is larger than in water and decreases with increasing cosolvent concentration; the solubility of $[Co(en)_3][Fe(CN)_6]$ as a function of acetonitrile concentration passes through a maximum. The values of $\Delta_{tr}G^0$ at 25°C evaluated for each solvent composition, along with the values of $\Delta_{tr}H^0$, $T\Delta_{tr}S^0$, and the values of the coefficients of Eq. (3), are listed in Tables 3 and 4. The reported data indicate that both investigated salts are

Table 3
Thermodynamic functions of transfer of $[Co(NH_3)_6][Fe(CN)_6]$ from water to water–organic mixtures (molality scale, 298.1 K) and the coefficients *a*, *b*, *c* of Eq. (3)

Wt%	$\Delta_{tr}G^0$/ kJ mol^{-1}	$\Delta_{tr}H^0$/ kJ mol^{-1}	$T\Delta_{tr}S^0$/ kJ mol^{-1}	a/ kJ mol^{-1}	b/ kJ mol^{-1} K^{-1}	c/ kJ mol^{-1} K^{-1}
			tert-C_4H_9OH			
10	2.2	8.9	6.7	−77.665	1.807	−0.270
20	4.4	−13	−17	−25.935	0.3509	−0.044
30	6.5	−12	−18	−550.03	12.15	−1.804
40	8.0	−11	−19	−457.16	10.09	−1.497
			CH_3CN			
10	−2.8	−38	−35	−325.95	6.575	−0.964
20	−1.9	−45	−43	−592.71	12.44	−1.836
30	−0.3	−50	−49	−816.16	17.38	−2.570
40	0.2	−51	−51	−509.66	10.47	−1.538

Table 4
Thermodynamic functions of transfer of $[Co(en)_3][Fe(CN)_6]$ from water to water–organic mixtures (molality scale, 298.1 K) and the coefficients *a*, *b*, *c* of Eq. (3)

Wt%	$\Delta_{tr}G^0$/ kJ mol^{-1}	$\Delta_{tr}H^0$/ kJ mol^{-1}	$T\Delta_{tr}S^0$/ kJ mol^{-1}	a/ kJ mol^{-1}	b/ kJ mol^{-1} K^{-1}	c/ kJ mol^{-1} K^{-1}
			tert-C_4H_9OH			
10	3.8	33	29	610.35	−13.06	1.935
20	7.3	22	15	361.25	−7.671	1.138
30	9.8	36	26	1385.8	−30.42	4.528
40	13	−8.5	−22	−121.14	2.603	−0.378
			CH_3CN			
10	−2.4	−15	−13	−23.599	0.227	−0.027
20	−2.6	−24	−21	−61.296	0.902	−0.124
30	−0.7	−32	−31	41.258	−1.517	0.241
40	1.6	−31	−33	−232.41	4.569	−0.665

increasingly destabilized with increasing concentration of *tert*-butyl alcohol and that they are stabilized at lower acetonitrile concentrations. However, this stabilization diminishes with increasing cosolvent concentration and at 40 wt% CH_3CN, a slight destabilization takes place.

In order to evaluate the single-ion values of the Gibbs energy of transfer, the data for $[(CH_3)_4N]_3[Fe(CN)_6]$ given in Ref. [7] have been used. The values of $\Delta_{tr}G^0$ for $(CH_3)_4N^+$ ion were taken from Refs. [8,9] and were used after conversion to the molality scale. The values for 10 and 30 wt% of CH_3CN were obtained by interpolation of the published data. For the Gibbs energy of transfer of $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$, the following equation holds

$$\Delta_{tr}G^0(Co^{3+}) = \Delta_{tr}G^0\{[Co]^{3+}[Fe]^{3-}\} - \Delta_{tr}G^0\{[(CH_3)_4N]_3[Fe(CN)_6] \\ + 3\Delta_{tr}G^0\{(CH_3)_4N^+\}$$

In this equation, $\Delta_{tr}G^0(Co^{3+})$ stands for the Gibbs energy of transfer of $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$, and $\Delta_{tr}G^0\{[Co]^{3+}[Fe]^{3-}\}$ for the Gibbs energy of transfer of $[Co(NH_3)_6][Fe(CN)_6]$ and $[Co(en)_3][Fe(CN)_6]$, respectively. All calculations of the single-ion transfer functions are based on the TATB reference electrolyte assumption. The values of the Gibbs energies of transfer for $[Fe(CN)_6]^{3-}$, $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ ions are summarized in Table 5. It follows from the reported data that the overall destabilization of both investigated complex salts in water–*tert*-butyl alcohol mixtures is mainly due to the destabilization of $[Co(NH_3)_6]^{3+}$ and/or $[Co(en)_3]^{3+}$ ions at the lowest cosolvent concentration, and to the destabilization of $[Fe(CN)_6]^{3-}$ ion for the transfer to the mixtures with higher content of *tert*-butyl alcohol. However, both $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ ions are destabilized in water–acetonitrile mixtures (with the exception of $[Co(NH_3)_6]^{3+}$ ion at highest cosolvent concentration).

Table 5
Gibbs energies of transfer, $\Delta_{tr}G^0$(kJ mol^{-1}), of $[Fe(CN)_6]^{3-}$, $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ ions from water to water–*tert*-butanol and water–acetonitrile mixtures (298.1 K, molality scale)

Wt%	$\Delta_{tr}G^0$		
	$[Fe(CN)_6]^{3-}$	$[Co(NH_3)_6]^{3+}$	$[Co(en)_3]^{3+}$
		tert-C_4H_9OH	
10	−3.5	5.7	7.3
20	6.3	−1.9	1.0
30	23	−16	−13
40	34	−27	−21
		CH_3CN	
10	−6.8	4.0	4.4
20	−5.8	3.9	3.2
30	−3.9	3.6	3.2
40	0.6	−0.4	1.0

The overall stabilization of both complex salts (again with the exception for 40 wt% of acetonitrile) is due to the stabilization of $[Fe(CN)_6]^{3-}$ ion in these media. Tables 3 and 4 show significant differences in the values of the enthalpies and entropies of transfer for the salts investigated for the mixtures water–*tert*-butyl alcohol. This different behaviour is evidently due to the different composition of the coordination spheres of the complex cations. This conclusion is in agreement with the single-ion values of $\Delta_{tr}G^0$ for $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ ions respectively (Table 5). However, the thermodynamic functions of transfer to water–acetonitrile mixtures show a certain similarity, i.e. $\Delta_{tr}H^0$ for both complex salts are negative and the transfer results in a large decrease in entropy. One possible explanation of the different behaviour of *tert*-butyl alcohol and acetonitrile is based on the different effect of these cosolvents on the cluster structure of water. *tert*-Butyl alcohol is known as a water-structure maker [10], i.e. with its increasing concentration in an aqueous mixture, the number of monomeric water molecules decreases which results in the dehydration of ions of the dissolved salts and, therefore, in their destabilization in these mixtures. Acetonitrile, is a water-structure breaker [11, 12] and increases the concentration of free, non-associated water molecules. There are enough monomeric water molecules in water–acetonitrile mixtures, so hydration is enhanced in these media. However, at higher concentrations the formation of hydrogen-bonded complexes, H_2O–CH_3CN, takes place [9,13]. It is evident that more effects are operating simultaneously in a water–acetonitrile mixture. At moderate cosolvent concentrations, the monomeric water molecules, liberated from clusters by the structure-breaking effect of acetonitrile, are immediately trapped in the associates CH_3CN–H_2O. These oppositely acting effects can also account for some observations concerning solubility and the thermodynamic transfer functions.

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