Activity Coefficients and Gibbs Energies of Transfer of Hexaamminecobalt(III) Hexacyanoferrate(III)

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The solubility of hexaamminecobalt(III) hexacyanoferrate(III) was measured in aqueous and aqueous—methanolic solutions of $NaClO_4$. The experimental mean activity coefficients, evaluated from these measurements are compared with those calculated with the aid of extended Debye—Hückel relations. From their temperature dependence the partial molar enthalpy and partial molar heat capacity have been obtained. The data on solubility in water—methanol mixtures served for the evaluation of Gibbs energies of transfer.

Hexaamminecobalt(III) hexacyanoferrate(III), *i.e.* $[Co(NH_3)_6][Fe(CN)_6]$ is only sparingly soluble in water and water—methanol solvent mixtures. The measurements of solubility of this salt together with the measurements of the solubility of hexaamminecobalt(III) oxalate in aqueous solutions of various electrolytes were published in the past [1—3]. The results of this investigation have been used for the evaluation of relative activity coefficients of the saturating salts. Hexaamminecobalt(III) hexacyanoferrate(III) is well suited to the solubility measurements because of the high kinetic stability of the complex ions which form this salt. The aim of the present work was to gain the experimental values of mean activity coefficients of the investigated complex salt in water as well as in water—methanol mixtures and to evaluate the Gibbs energies of transfer from water to these mixed solvents.

EXPERIMENTAL

Hexaamminecobalt(III) hexacyanoferrate(III) was prepared by precipitation of hexaamminecobalt(III) chloride with an aqueous solution of potassium hexacyanoferrate. $[Co(NH_3)_6]Cl_3$ and $K_3[Fe(CN)_6]$ were products of the British Drug Houses and Lachema, Brno, respectively. Analysis gave the following results: for $[Co(NH_3)_6][Fe(CN)_6]$ (M_r = 373.07) w_i(calc.): 19.31 % C, 4.86 % H, 45.05 % N; w_i(found): 19.0 % C, 4.7 % H, 44.7 % N. All the other chemicals used were of anal. grade. Methanol was distilled prior to use, doubly distilled water was used throughout. The solutions were made up by mass in all cases.

In the measuring procedure an excess of solid complex was stirred with a solution of $NaClO_4$ in water or in water—methanol mixtures for 4 h in a jacketed vessel kept at (25.0 ± 0.05) °C. Longer equilibration time (48 h) yielded the same result. A sample of the saturated solution was rapidly filtered through a sintered glass and analyzed spectrophotometrically. The absorption spectra of the sample were measured by means of the spectrophotometer Specord UV VIS, the concentration of the saturating salt was determined by measurements of the absorbance using Spekol EK 5 (both Zeiss, Jena). At least three independent measurements for each sample were performed, the relative error in solubility did not exceed 5 %.

RESULTS AND DISCUSSION

The absorption spectra of potassium hexacyanoferrate(III) and hexaamminecobalt(III) chloride are presented in Fig. 1. It is evident from the figure that the absorption of hexacyanoferrate anion is intense

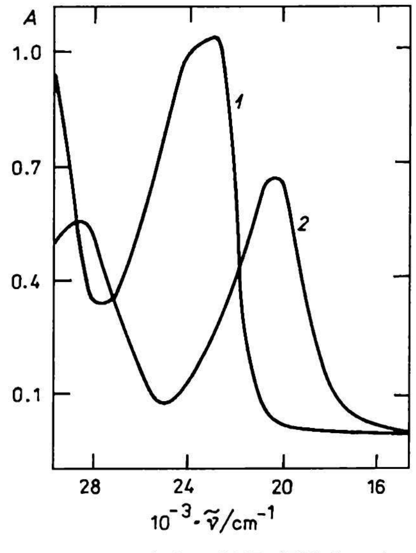

Fig. 1. Absorption curve of *1.* $m(K_3[Fe(CN)_6])$ = 1 × 10^{-3} mol kg^{-1}; *2.* $m([Co(NH_3)_6]Cl_3)$ = 2.66 × 10^{-3} mol kg^{-1}; 4.00 cm cell path.

Table 1. Solubilities *S* of $[Co(NH_3)_6][Fe(CN)_6]$ in Aqueous Solutions of $NaClO_4$ at Various Temperatures

$m(NaClO_4)$	$10^5\ S$/(mol kg^{-1})				
mol kg^{-1}	*T*/K				
	288.15^a	298.15^b	308.15^c	318.15^d	328.15^e
0	2.09 ± 0.03	3.70 ± 0.10	4.56 ± 0.18	7.03 ± 0.23	9.31 ± 0.50
0.01	4.56 ± 0.22	6.90 ± 0.12	9.12 ± 0.23	12.6 ± 0.1	16.3 ± 0.4
0.02	5.89 ± 0.10	9.06 ± 0.22	12.1 ± 0.2	16.7 ± 0.3	21.8 ± 0.4
0.03	7.22 ± 0.15	10.4 ± 0.2	15.0 ± 0.2	20.3 ± 0.2	27.2 ± 0.6
0.05	11.3 ± 0.01	14.5 ± 0.1	20.5 ± 0.1	27.4 ± 0.5	35.7 ± 0.1

The values of solubility extrapolated to zero ionic strength, $\{S_0\} = S_0/(\text{mol kg}^{-1})$: *a*) $\{S_0\} = (1.82 \pm 0.09) \times 10^{-5}$; *b*) $\{S_0\} = (3.14 \pm 0.11) \times 10^{-5}$; *c*) $\{S_0\} = (3.83 \pm 0.03) \times 10^{-5}$; *d*) $\{S_0\} = (5.73 \pm 0.05) \times 10^{-5}$; *e*) $\{S_0\} = (7.32 \pm 0.06) \times 10^{-5}$.

(extinction coefficient at the wavelength of absorption maximum is 1015 kg mol^{-1} cm^{-1}), however, the absorption of $[Co(NH_3)_6]^{3+}$ ion cannot be neglected at this wavelength, its extinction coefficient being 18 kg mol^{-1} cm^{-1}. The molality of the saturating salt was therefore evaluated from the measured absorbance by an iterative procedure including the absorption of hexaammine ion.

The solubilities of hexaamminecobalt(III) hexacyanoferrate(III) in aqueous solutions of $NaClO_4$ at various temperatures are reported in Table 1. It is seen from the table that the solubility of the saturating salt increrases with increasing ionic strength at all experimental temperatures. For the experimental data the Debye—Hückel law in the extended form (*1*) is obeyed.

$$\log (S/S_0) = \alpha\{I\}^{1/2}/(1 + \beta\{I\}^{1/2}) \qquad (1)$$

S being the solubility at a given ionic strength, S_0 its value extrapolated to zero ionic strength, α includes the Debye—Hückel constant *A* and the charge product of ions of the saturating salt, β contains the Debye—Hückel constant *B* and the distance of the closest approach *a*. For the purpose of extrapolation of the solubility to zero ionic strength eqn (*1*) was used with β = 1 kg$^{1/2}$ mol$^{-1/2}$. The dependence $\log (S/S_0) = f[\{I\}^{1/2}/(1 + \{I\}^{1/2})]$ was linear and enabled the extrapolation procedure. It is interesting to compare the experimental values of mean activity coefficients with the calculated ones evaluated by means of various relationships based on Debye—Hückel theory. The experimental and calculated values of $\gamma_\pm$ are reported in Table 2. $(\gamma_\pm)_{calc,a}$ are the values calculated with the use of eqn (*1*) where $\alpha = A\,|z_+z_-| = 9A$, β = 1 kg$^{1/2}$ mol$^{-1/2}$, $(\gamma_\pm)_{calc,b}$ were calculated by means of eqn (*1*) when β = 1.5 kg$^{1/2}$ mol$^{-1/2}$ (McInnes approximation [4]), for the calculation of $(\gamma_\pm)_{calc,c}$ the extended relationship (*2*) with the linear term in $\{I\}$ has been used [5].

Table 2. Experimental and Calculated Mean Activity Coefficients, $(\gamma_\pm)_{exp}$, $(\gamma_\pm)_{calc}$ of $[Co(NH_3)_6][Fe(CN)_6]$ in Aqueous $NaClO_4$ Solutions at 298.15 K

$m(NaClO_4)$ mol kg^{-1}	$(\gamma_\pm)_{exp}$	$(\gamma_\pm)_{calc}{}^a$	$(\gamma_\pm)_{calc}{}^b$	$(\gamma_\pm)_{calc}{}^c$
0	0.848	0.827	0.831	0.828
0.01	0.455	0.367	0.384	0.375
0.02	0.347	0.259	0.280	0.271
0.03	0.303	0.206	0.230	0.220
0.05	0.216	0.140	0.166	0.156

a) and *b*) The values obtained by means of eqn (*1*) (see the text), *c*) with the use of eqn (*2*).

$$-\log \gamma_\pm = A\,|z_+z_-|\,\{I\}^{1/2}/(1 + \{I\}^{1/2}) - 0.1\,|z_+z_-|\,\{I\} \qquad (2)$$

It can be deduced from Table 2 that the best agreement between calculated and experimental values has been achieved when McInnes relationship was used. It is also seen from the table that the experimental values of the mean activity coefficients are larger than the calculated ones in pure water and in all investigated $NaClO_4$ solutions, the difference $(\gamma_\pm)_{exp} - (\gamma_\pm)_{calc}$ being more considerable at higher perchlorate concentrations. This observation is in harmony with the conclusions of the theory of nonelectrostatic contributions to the activity coefficients of electrolytes [6]. This contribution is especially important in the solutions where for relative size *r* of the solute ions and solvent molecules it holds *r* >> 1. With regard to the fact that both cation and anion of the investigated salt are large ions, the above-mentioned condition is well fulfilled. However, the role of $NaClO_4$ as water structure breaker cannot be omitted in such considerations [7]. It is interesting that the experimental value of the slope α_{exp} of the dependence $\log (S/S_0) = f[\{I\}^{1/2}/(1 + \{I\}^{1/2})]$ has a value 3.597 kg$^{1/2}$ mol$^{-1/2}$ whereas the calculated value α_{calc}= 4.584 kg$^{1/2}$ mol$^{-1/2}$. The lower experimental value can be explained using the assumption on ion—pair formation which diminishes the effective charge product of the saturating salt. The effect of temperature on the mean activity coefficient is expressed by the following relationship

$$(\partial \ln\gamma_\pm/\partial T)_p = -\bar{L}/2RT^2 \qquad (3)$$

$\bar{L}$ is the relative partial molar enthalpy of the electrolyte. To integrate eqn (*3*) one must consider the fact that $\bar{L}$ is temperature-dependent even over a narrow range of temperature. This dependence defines the partial molar heat capacity, $\bar{J}$

$$\bar{J} = (\partial \bar{L} / \partial T)_p \qquad (4)$$

For a temperature interval from the reference temperature 298.15 K to the temperature T the relationship (5) can be derived [8]

$$\log \gamma_{\pm}(T) = \log \gamma_{\pm}(298.15\ \text{K}) + Y' \bar{L}(298.15\ \text{K}) - \\ - Z' \bar{J}(298.15\ \text{K}) \qquad (5)$$

where $\{Y'\} = 3.503 \times 10^{-4}\ \{(298.15\ \text{K} - T)/T\}$, $Z' = 298.15\ (Y') + 0.2406 \log (T/298.15\ \text{K})$.

For the lowest experimental ionic strength, corresponding to the saturated solution of the complex salt, *i.e.* $m(\text{NaClO}_4) = 0$, the relative partial molar enthalpy $\bar{L} = (9.5 \pm 1.8)$ kJ mol^{-1}. With respect to the customary precision of our experiments, the partial molar heat capacity could be only estimated. The estimated value is – 0.3 kJ mol^{-1} K^{-1}. Relatively few data exist in the literature concerning the temperature dependence of the activity coefficients, the corresponding data for the complex salts seem to be absent. On the basis of the studies of simple electrolytes [8] it can be deduced that the absolute value of $\bar{L}$ increases with the ionic diameter as well as with the ionic charge. According to this the value of $\bar{L}$, obtained in the present work, seems to be reasonable.

The solubility of $[\text{Co(NH}_3)_6][\text{Fe(CN)}_6]$ has been measured as a function of perchlorate concentration in binary mixtures of water with methanol. The results of these measurements are reported in Table 3. Eqn (*1*) was obeyed also for mixed solvents. From the linear dependence $\log (S/S_0) = \text{f}[\{I\}^{1/2}/(1 + \{I\}^{1/2})]$ the values extrapolated to zero ionic strength have been obtained. The solubility data in water and aqueous—methanolic mixtures enabled the evaluation of the Gibbs energies of transfer, $\Delta G^{\circ}_{\text{tr}}$ of the saturating salt from water to the examined solvent mixtures. According to the basic thermodynamic relations the eqn (*6*) can be written relating the transfer function with the solubility products of the saturating salt in water, K_s(w) and in a mixed solvent, K_s(mix)

$$\Delta G^{\circ}_{\text{tr}} = RT \ln [K_s(\text{w})/K_s(\text{mix})] \qquad (6)$$

Using the solubilities in water, S^{w}, and in a mixed solvent, S^{mix}, eqn (*7*) can be written for the Gibbs energy of transfer.

$$\Delta G^{\circ}_{\text{tr}} = 2\ RT \ln [(S^{\text{w}}/S^{\text{mix}})\ (\gamma_{\pm}(\text{w})/\gamma_{\pm}(\text{mix}))] \qquad (7)$$

$\gamma_{\pm}$(w) and $\gamma_{\pm}$(mix) are the mean molar activity coefficients. The values of $\Delta G^{\circ}_{\text{tr}}$ corresponding to the transfer of $[\text{Co(NH}_3)_6][\text{Fe(CN)}_6]$ from water to the binary mixtures of water with methanol are reported in Table 4. We can see that with increasing concentration of methanol the Gibbs energy of transfer becomes more positive, *i.e.* the complex salt is increasingly destabilized in a mixed solvent with increasing concentration of organic cosolvent. This behaviour of the complex salt is evidently connected with the hydrophilic character of both complex ions of this electrolyte.

Table 3. Solubilities S of $[\text{Co(NH}_3)_6][\text{Fe(CN)}_6]$ in Water—Methanol Solvent Mixtures and at Various NaClO_4 Concentrations at 298.15 K

$\frac{m(\text{NaClO}_4)}{\text{mol kg}^{-1}}$	$\frac{10^5\ S}{\text{mol kg}^{-1}}$	$\frac{m(\text{NaClO}_4)}{\text{mol kg}^{-1}}$	$\frac{10^5\ S}{\text{mol kg}^{-1}}$
10 mass % CH_3OH^a		30 mass % CH_3OH^c	
0	1.42 ± 0.05	0	0.48 ± 0.05
0.01	3.32 ± 0.08	0.01	1.23 ± 0.01
0.02	4.65 ± 0.08	0.02	1.61 ± 0.02
0.03	6.08 ± 0.02	0.03	2.28 ± 0.05
0.05	8.83 ± 0.10	0.05	3.13 ± 0.14
20 mass %^{b}		40 mass %^{d}	
0	0.68 ± 0.03	0	0.15 ± 0.01
0.01	1.80 ± 0.05	0.01	0.57 ± 0.08
0.02	2.66 ± 0.05	0.02	0.87 ± 0.01
0.03	3.51 ± 0.04	0.03	1.23 ± 0.04
0.05	5.22 ± 0.29	0.05	1.61 ± 0.24

The values of solubility extrapolated to zero ionic strength, $\{S_0\} = S_0/(\text{mol kg}^{-1})$: *a*) $\{S_0\} = (1.27 \pm 0.01) \times 10^{-5}$; *b*) $\{S_0\} = (0.62 \pm 0.01) \times 10^{-5}$; *c*) $\{S_0\} = (0.45 \pm 0.02) \times 10^{-5}$; *d*) $\{S_0\} = (0.15 \pm 0.02) \times 10^{-5}$.

Table 4. Gibbs Energies of Transfer, $\Delta G^{\circ}_{\text{tr}}$ (Molality Scale), of $[\text{Co(NH}_3)_6][\text{Fe(CN)}_6]$ from Water to the Water—Methanol Mixtures at 298.15 K

mass % CH_3OH	$S^{\text{w}}/S^{\text{mix}}$	$\gamma_{\pm}(\text{w})/\gamma_{\pm}(\text{mix})$	$\Delta G^{\circ}_{\text{tr}}/(\text{kJ mol}^{-1})$
10	2.6	0.95	4.5
20	5.42	0.93	8.0
30	7.80	0.90	9.7
40	24.4	0.83	14.9

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