ACTIVITY COEFFICIENTS OF TRIS(ETHYLENEDIAMINE)COBALT(III) HEXACYANOFERRATE(III) IN WATER AND MIXED WATER–ALCOHOL SOLVENTS

Vladislav HOLBA
Department of Physical Chemistry,
Comenius University, 842 15 Bratislava, The Slovak Republic

Received August 10, 1992
Accepted December 12, 1992

The solubility of tris(ethylenediamine)cobalt(III) haxacyanoferrate(III) were measured in aqueous solutions of $NaClO_4$, NaCl, KCl, KBr, K_2SO_4, $MgSO_4$, $(CH_3)_4NBr$, $(C_2H_5)_4NBr$, $(1\text{-}C_3H_7)_4NBr$, and $(1\text{-}C_4H_9)_4NBr$, as well as in the solutions of $NaClO_4$ in mixtures of water with methanol and *tert*-butyl alcohol. The experimental mean actvity coefficients are compared with theoretical ones evaluated with the aid of extended Debye–Hückel relation. From the solubilities in water and in water–alcoholic solvents the thermodynamic transfer functions of the saturating salt were calculated.

Solubility measurements of sparingly soluble electrolytes with higher charged ions in the presence of various salts are well suited to the detection of specific interaction effects. These are often interpreted in terms of specific interaction parameters, distance of closest approach or formation of ion pairs[1 – 4]. The measurements of the effect of organic cosolvents in mixed aqueous–alcoholic solvents on solubility together with the determination of activity coefficients of the saturating salt in these media enable the evaluation of its thermodynamic transfer functions[5]. Tris(ethylenediamine)cobalt(III) hexacyanoferrate(III) was chosen for solubility studies because its ions are thermodynamically and kinetically well stable, and its solubility can be determined spectrophotometrically due to the high extinction coefficient of the hexacyanoferrate(III) ion in the visible region. Because the studied salt is a 3-3 electrolyte, the specific effects of ions of the supporting electrolytes can be expected.

EXPERIMENTAL

The salt $[Co(en)_3][Fe(CN)_6]$ (en = ethylenediamine) was prepared by precipitation of the saturated solution of $K_3[Fe(CN)_6]$ (Lachema, Brno, reagent grade) with the saturated solution of $[Co(en)_3]Br_3$. H_2O. The last complex salt was prepared according to ref.[6]. The precipitate was filtered, washed with cold water and dried at 110 °C under vacuum. All other chemicals were of reagent grade, methanol and *tert*-butyl alcohol have been distilled prior to use. Double distilled water was used throughout. All solutions were prepared by mass.

The solubilities were determined by stirring the tris(ethylenediamine)cobalt(III) hexacyanoferrate(III) together with the supporting electrolyte in a jacketted vessel thermostatted to 25 ± 0.05 °C. The equilibrium between the solid phase and the saturated solution was achieved after 6 h of stirring. Longer equilibration time (10 h) yielded the same result. The concentration of the saturating salt in the equilibrated solution was determined by measurements of the absorbance at 420 nm where $[Fe(CN)_6]^{3-}$ ion has a maximum with the extinction coefficient 1 015 mol^{-1} kg cm^{-1}. However, the absorption of $[Co(en)_3]^{3+}$ ion cannot be neglected at this wavelength (Fig. 1), its extinction coefficient being 30 mol^{-1} kg cm^{-1}. Therefore the appropriate correction was introduced in the calculations of the concentrations of saturating salt. The measurements of the absorbance were performed using Specord UV-VIS spectrophotometer (Zeiss, Jena).

RESULTS AND DISCUSSION

The solubilities of tris(ethylediamine)cobalt(III) hexacyanoferrate(III) in aqueous solutions of different supporting electrolytes are reported in Table I. The solubility of $[Co(en)_3][Fe(CN)_6]$ at 25 °C in pure water was found to be (4.56 ± 0.12) . 10^{-4} mol kg^{-1}. It is seen from Table I that the solubilty of the saturating salt increases with increasing ionic strength in all investigated solutions. For the experimental data the Debye–Hückel law in the extended form (*1*) is obeyed

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

where S is 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 closest approach a. The dependence $\log (S/S_0) = f\{\sqrt{I}/(1 + \sqrt{I})\}$ was in all cases linear and enabled the extrapolation of S (the ionic strength did not exceed the value of 0.055 mol kg^{-1} in these experiments). The mean value of solubility of the saturating salt, extrapolated to zero ionic strength calculated from the data of ten supporting electro-

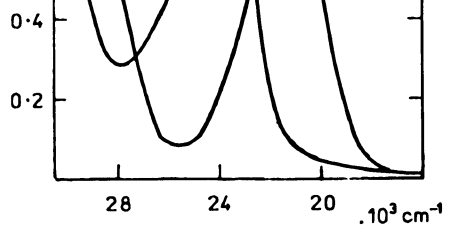

FIG. 1

Absorption curve of *1* $[Co(en)_3][Fe(CN)_6]$ 4 . 10^{-4} mol kg^{-1}, 2 cm cell path; *2* $[Co(en)_3]Br_3$ 1 . 10^{-2} mol kg^{-1}, 1 cm cell path; aqueous solutions lytes, reported in Table I, is $\langle S_0 \rangle = (2.68 \pm 0.17) \,.\, 10^{-4}$ mol kg^{-1}. The values of the slope α fall into three categories. For supporting electrolytes $NaClO_4$, NaCl, KCl and KBr, $\alpha_{exp} = 3.15 \pm 0.11$, for used quaternary ammonium salts $\alpha_{exp} = 3.93 \pm 0.10$, for K_2SO_4 and $MgSO_4$ $\alpha_{exp} = 4.34 \pm 0.25$. The theoretical value at 25 °C, resulting from Debye–Hückel theory, $\alpha_{theor} = A \mid z_A z_B \mid = 4.584$ kg$^{1/2}$ mol$^{-1/2}$. The lower experimental values in first two categories of supporting electrolytes could be explained using the assumption on ion-pair formation which diminishes the effective charge of the ions of the saturating salt. However, the experimental slope in the solutions of K_2SO_4 and $MgSO_4$ is within the experimental error identical with the theoretical one. This fact is at variance

TABLE I

Solubilities, S, of $[Co(en_3)][Fe(CN)_6]$ in aqueous solutions of supporting electrolytes of various molalities, m, at 25 °C

m mol kg^{-1}	$S \,.\, 10^4$ mol kg^{-1}	m mol kg^{-1}	$S \,.\, 10^4$ mol kg^{-1}	m mol kg^{-1}	$S \,.\, 10^4$ mol kg^{-1}
$NaClO_4$		KBr		$(1\text{-}C_4H_9)_4NBr$	
0.002	4.86 ± 0.07	0.005	5.00 ± 0.17	0.003	4.83 ± 0.20
0.004	5.23 ± 0.10	0.010	6.52 ± 0.22	0.005	5.76 ± 0.24
0.010	6.09 ± 0.26	0.020	7.62 ± 0.06	0.010	7.13 ± 0.34
0.015	7.08 ± 0.21	0.028	9.53 ± 0.56	0.020	9.13 ± 0.15
0.020	7.67 ± 0.33	0.035	10.6 ± 0.1	0.035	12.7 ± 0.3
0.030	8.69 ± 0.08	$(CH_3)_4NBr$		K_2SO_4	
0.040	9.93 ± 0.19	0.005	6.01 ± 0.09	0.001	5.86 ± 0.21
0.045	10.33 ± 0.1	0.010	6.91 ± 0.17	0.002	7.10 ± 0.13
NaCl		0.020	9.58 ± 0.35	0.004	9.20 ± 0.12
0.004	5.12 ± 0.15	0.035	13.1 ± 0.2	0.005	10.3 ± 0.1
0.006	5.59 ± 0.19	$(C_2H_5)_4NBr$		0.006	12.1 ± 0.3
0.010	6.29 ± 0.22	0.006	6.34 ± 0.20	0.008	12.9 ± 0.2
0.020	7.96 ± 0.21	0.010	7.38 ± 0.10	0.010	14.4 ± 0.3
0.035	10.3 ± 0.3	0.020	9.80 ± 0.35	$MgSO_4$	
0.045	11.4 ± 0.1	0.035	13.9 ± 0.3	0.001	5.96 ± 0.10
KCl		$(1\text{-}C_3H_7)_4NBr$		0.0015	6.23 ± 0.47
0.005	5.23 ± 0.03	0.005	5.31 ± 0.34	0.0025	7.57 ± 0.20
0.010	6.01 ± 0.08	0.010	6.65 ± 0.22	0.003	8.37 ± 0.02
0.025	8.82 ± 0.06	0.020	8.92 ± 0.06	0.005	10.9 ± 0.5
0.035	10.7 ± 0.3	0.035	12.4 ± 0.1	0.0075	12.5 ± 0.1
0.045	11.6 ± 0.1	–		0.010	14.7 ± 0.2

with the theory of ion association which leads to the conclusion that increasing ionic charge enhances the ion-pair formation[7]. The tetraalkylammonium bromides differ clearly from inorganic 1-1 electrolytes used, giving a bigger increase in solubility. This behaviour is evidently more due to the hydrophobic character of these cations than to their larger size[3].

The specificity of interionic interactions is manifested in the values of β in relationship (*1*), as well as in the values of the distance of closest approach a, evaluated from $\beta = a\,B$, $B = 3.29 \,.\, 10^{-10}$ $\text{mol}^{-1/2}\ \text{m}^{-1}\ \text{kg}^{1/2}$. The values of β were calculated using the experimental values of α for given supporting electrolytes. In $NaClO_4$ $\beta = 1.88 \pm 0.18$ which corresponds to the value of $a = 0.57$ nm, in all other uni-univalent inorganic salts $\beta = 1.35 \pm 0.74$, $a = 0.41$ nm. In the quaternary ammonium bromides $\beta = 1.04 \pm 0.22$, $a = 0.32$ nm, in K_2SO_4 $\beta = 0.54 \pm 0.16$, $a = 0.16$ nm, and in $MgSO_4$ $\beta = 1.49 \pm 0.13$, $a = 0.45$ nm.

It is interesting to compare the experimental value of mean activity coefficients with the theoretical one given by the Eq. (*2*) (see ref.[8])

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

where A is the Debye–Hückel constant, $\gamma_\pm = S_0/S$. Experimental values of $\gamma_\pm$ in the solutions of different supporting electrolytes with the ionic strength 0.01 mol kg^{-1} at 25 °C are reported in Table II. The theoretical value at this ionic strength according to the Eq. (*2*) is 0.3911. We see that in the solutions of uni-univalent supporting electrolytes with inorganic anions, excepting KBr, $(\gamma_\pm)_{exp} > (\gamma_\pm)_{theor}$, in the solutions of KBr and those of quaternary ammonium bromides $(\gamma_\pm)_{exp}$ is within the experimental error identical with its theoretical value, and in the solutions of investigated sulfates $(\gamma_\pm)_{exp} << (\gamma_\pm)_{theor}$.

TABLE II
Experimental values of the mean activity coefficients, $(\gamma_\pm)_{exp}$ in 0.01 mol kg^{-1} solutions of supporting electrolytes

Supporting electrolyte	$(\gamma_\pm)_{exp}$	Supporting electrolyte	$(\gamma_\pm)_{exp}$
$NaClO_4$	0.440	$(C_2H_5)_4NBr$	0.362
$NaCl$	0.424	$(1\text{-}C_3H_7)_4NBr$	0.401
KCl	0.444	$(1\text{-}C_4H_9)_4NBr$	0.375
KBr	0.409	K_2SO_4	0.185
$(CH_3)_4NBr$	0.386	$MgSO_4$	0.181

Despite of the fact that the saturating salt is formed by relatively large ions, it is hardly to explain the observed trends in activity coefficients using the idea of non-electrostatic contribution[9]. On the other hand, the effect of used supporting electrolytes on the activity coefficients of the saturating salt can be correlated with their influence on the cluster structure of water. Numerous experiments showed that ClO_4^- ions are effective structure breakers, i. e. they lower the number of hydrogen bonds between water molecules, SO_4^{2-} ions act in opposite direction[10]. The placing of $NaClO_4$, K_2SO_4, and

TABLE III

Solubilities, S, of $[Co(en)_3][Fe(CN)_6]$ in water–alcohol solvent mixtures and various $NaClO_4$ molalities, m, at 25 °C

m_{NaClO_4} mol kg^{-1}	$S \cdot 10^4$ mol kg^{-1}	m_{NaClO_4} mol kg^{-1}	$S \cdot 10^4$ mol kg^{-1}
	10 wt.% CH_3OH		10 wt.% *tert*-C_4H_9OH
0	2.75 ± 0.06	0	1.94 ± 0.06
0.003	3.58 ± 0.50	0.010	3.54 ± 0.22
0.005	3.97 ± 0.12	0.030	5.26 ± 0.09
0.010	4.85 ± 0.05	0.050	6.76 ± 0.03
0.050	8.58 ± 0.31	0.075	9.00 ± 0.10
	20 wt.% CH_3OH		20 wt.% *tert*-C_4H_9OH
0	1.78 ± 0.05	0	0.80 ± 0.05
0.005	2.28 ± 0.15	0.010	1.71 ± 0.15
0.010	2.47 ± 0.09	0.030	2.65 ± 0.06
0.030	3.65 ± 0.06	0.050	3.70 ± 0.12
0.050	4.85 ± 0.03	0.075	4.76 ± 0.18
	30 wt.% CH_3OH		30 wt.% *tert*-C_4H_9OH
0	1.53 ± 0.12	0	0.27 ± 0.03
0.010	1.91 ± 0.13	0.010	1.00 ± 0.05
0.030	2.59 ± 0.07	0.030	1.14 ± 0.02
0.050	3.51 ± 0.08	0.050	1.96 ± 0.09
0.075	4.26 ± 0.10	0.075	2.42 ± 0.06
	40 wt.% CH_3OH		
0	1.38 ± 0.15		
0.010	1.84 ± 0.05		
0.030	2.80 ± 0.19		
0.050	3.41 ± 0.19		
0.075	3.91 ± 0.29		

$MgSO_4$ in the Table II suggests such interpretation. However, all experimental results cannot be explained in this way. It is evident that the resulting effect of supporting electrolytes on the activity coefficient of the saturating salt is a consequence of several simultaneously operating ion–ion and ion–solvent interactions.

The solubility of $[Co(en)_3][Fe(CN)_6]$ has been measured as a function of sodium perchlorate concentration in binary mixed solvents water–methanol and water–*tert*-butyl alcohol. The results of these measurements are reported in Table III. Equation (*1*) was obeyed also for mixed solvents, the dependence $\log (S/S_0) = f\,\{\sqrt{I}/(1 + \sqrt{I})\}$ was linear and enabled to obtain the values of solubility extrapolated to zero ionic strength. S_0 for 10, 20, 30, and 40 wt.% of CH_3OH are $(2.04 \pm 0.11) \cdot 10^{-4}$, $(1.35 \pm 0.06) \cdot 10^{-4}$, $(1.17 \pm 0.09) \cdot 10^{-4}$, and $(1.10 \pm 0.05) \cdot 10^{-4}$ mol kg^{-1}, its values for 10, 20, and 30 wt.% of *tert*-C_4H_9OH are $(1.45 \pm 0.06) \cdot 10^{-4}$, $(0.66 \pm 0.04) \cdot 10^{-4}$, and $(0.23 \pm 0.02) \cdot 10^{-4}$ mol kg^{-1}, respectively. The solubility data in water and in aqueous–alcoholic solvents enable the evaluation of Gibbs free energy of transfer, ΔG_t^0, of the saturating salt from water to the examined solvent mixtures. According to the basic thermodynamic relations the Eq. (*3*) holds between ΔG_t^0 and the solubility products of the saturating salt in water, K_S^w, and in a mixed solvent, K_S^{mix}

$$\Delta G_t^0 = R\,T \ln (K_S^w/K_S^{mix}) \,. \tag{3}$$

Using the solubilities in water and in the mixed solvent, S^w, S^{mix}, we have for ΔG_t^0

$$\Delta G_t^0 = 2\,R\,T \ln \{(S^w/S^{mix})\,(\gamma_\pm^w/\gamma_\pm^{mix})\} \,, \tag{4}$$

TABLE IV

Gibbs energies of transfer, ΔG_t^0, of $[Co(en)_3][Fe(CN_6)]$ from water to the water–methanol and water–*tert*-butyl alcohol mixtures

Alcohol, wt.%	S^w/S^{mix}	$\gamma_\pm^w/\gamma_\pm^{mix}$	ΔG_t^0 kJ mol^{-1}
	CH_3OH		
10	1.66	0.79	1.34
20	2.56	0.77	1.38
30	2.98	0.76	4.09
40	3.30	0.73	4.39
	tert-C_4H_9OH		
10	2.35	0.78	3.03
20	5.70	0.71	6.93
30	16.9	0.69	12.1

$\gamma_{\pm}^{w}$ and $\gamma_{\pm}^{mix}$ are the corresponding activity coefficients. The values of ΔG_t^0 due to the transfer of the saturating salt from water to the binary mixtures water–methanol and water–*tert*-butyl alcohol are reported in Table IV. Together with the values of ΔG_t^0 for $[Co(en)_3][Fe(CN)_6]$ the values for the ions $[Co(en)_3]^{3+}$ and $[Fe(CN)_6]^{3-}$ were evaluated from the measured solubility of $[Co(en)_3]I_3$ in water and water–methanol mixtures[11]. The values of transfer function for I^- ion, based on TATB assumption, were taken from ref.[12]. For transfer into 20 wt.% CH_3OH the values of ΔG_t^0 $\{[Co(en)_3]^{3+}\}$ and ΔG_t^0 $\{[Fe(CN)_6]^{3-}\}$ in kJ mol^{-1} are 2.89 and 0.49, for transfer into 40 wt.% CH_3OH are 4.68 and −0.29, respectively.

REFERENCES

1. Dvořák J., Koryta J.: *Elektrochemie*, p. 57. Academia, Praha 1983.
2. Guggenheim E. A., Prue M. A.: *Fiziko-khimicheskie raschoty*, p. 218. Izdatelstvo Inostrannoi Literatury, Moscow 1958.
3. Ferranti F., Nunez Delgado J., Indelli A.: Electrochim. Acta *24*, 115 (1979).
4. Arsuaga J. M., Caceres-Alonso M., Castellanos M. A., Nunez J.: J. Solution Chem. *18*, 379 (1989).
5. Holba V., Grančičová O.: Chem. Listy *79*, 449 (1985).
6. Brauer G.: *Rukovodstvo po preparativnoi neorganicheskoi khimii*, p. 620. Izdatelstvo Inostrannoi Literatury, Moscow 1956.
7. Petrucci S.: *Ionic Interactions*, Vol. I, p. 117. Academic Press, New York 1971.
8. Robinson R. A., Stokes R. H.: *Rastvory elektrolitov*, p. 264. Izdatelstvo Inostrannoi Literatury, Moscow 1963.
9. Conway B. E. in: *Activity Coefficients in Electrolyte Solutions* (R. M. Pytkowicz, Ed.), Vol. I, p. 95. RCR Press, Boca Raton Fl. 1979.
10. Holba V.: Collect. Czech. Chem. Commun. *47*, 2484 (1982).
11. Holba V.: Unpublished results.
12. Abraham M. H., Hill T., Ling H. C., Schulz R., Watt R. A. C.: J. Chem. Soc., Faraday Trans. 1 *80*, 489 (1984).

Translated by the author.