

SOLUBILITY OF TRIS(ETHYLENEDIAMINE)CHROMIUM(III) AND HEXAUREACHROMIUM(III) HEXACYANOFERRATES(III) IN WATER AND MIXED WATER-ORGANIC SOLVENTS

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The solubilities of tris(ethylenediamine)chromium(III) and hexa(urea)chromium(III) hexacyanoferrates(III) in aqueous solutions of different supporting electrolytes as well as in binary mixtures of water with methanol, *tert*-butyl alcohol and acetonitrile were measured at 25 °C. The experimental data have been used to evaluate the activity coefficients of the saturating salts in water and their Gibbs energies of transfer from water into the binary mixtures investigated.

The measurements of solubility of sparingly soluble complex salts were performed in the past in order to obtain the values of the activity coefficients and the thermodynamic transfer functions¹⁻³. The measured values of the Gibbs energies of transfer of the studied salts and their ions from water into a binary water-organic solvent enable a deeper insight in the nature of solute-solvent interactions. The informations obtained can be used in the interpretation of medium effect on reactivity of investigated compounds.

In the present work we report the solubility of $[\text{Cr}(\text{en})_3][\text{Fe}(\text{CN})_6]$ (en = ethylenediamine) and $[\text{Cr}(\text{urea})_6][\text{Fe}(\text{CN})_6]$ (urea = $\text{H}_4\text{N}_2\text{CO}$) in aqueous solutions of different electrolytes as well as in binary mixtures of water with methanol, *tert*-butyl alcohol and acetonitrile at 25 °C. The aim of our work is to determine the mean activity coefficients of investigated salts (from solubility data in water) and to evaluate the Gibbs energies of transfer of the salts and of the complex ions $[\text{Cr}(\text{en})_3]^{3+}$ and $[\text{Cr}(\text{urea})_6]^{3+}$ from measurements in water-organic solvent mixtures.

EXPERIMENTAL

Chemicals. Tris(ethylenediamine)chromium(III) hexacyanoferrate(III) and hexa(urea)chromium(III) hexacyanoferrate(III) were prepared by precipitation of the saturated solutions of the corresponding chlorides with a saturated solution of potassium hexacyanoferrate(III). Analysis with the aid of Erba Science 1106 automatic analyzer gave the following results: For $[\text{Cr}(\text{en})_3][\text{Fe}(\text{CN})_6] \cdot 2 \text{H}_2\text{O}$ (480.28) calculated: 30.01% C, 5.88% H, 35.00% N; found: 29.90% C, 5.42% H, 35.23% N. For $[\text{Cr}(\text{H}_4\text{N}_2\text{CO})_6][\text{Fe}(\text{CN})_6] \cdot \text{H}_2\text{O}$ (642.30) calculated: 22.42% C, 4.08% H, 39.25% N; found: 21.81% C, 3.69% H, 38.95% N. $[\text{Cr}(\text{en})_3]\text{Cl}_3 \cdot 3.5 \text{H}_2\text{O}$ and $[\text{Cr}(\text{urea})_6]\text{Cl}_3 \cdot 3 \text{H}_2\text{O}$ were prepared as described

in the literature⁴. All the other salts were Merck, products of reagent grade. Bidistilled water was used throughout.

Solubility measurements. The solubilities were determined by stirring the investigated complex salts together with the supporting electrolyte and/or organic cosolvent in a jacketed vessel kept at 25 ± 0.05 °C. The equilibrium between the solid phase and the saturated solution was achieved after 4 h of stirring. In order to assure that the aquation of the complex cations does not influence the solubility, the measurements have been performed using the mixing of the solutions by ultrasound as described in ref.³. The sonication lasted only 360 s so that the aquation, which is at 25 °C very slow⁵, could not proceed to a measurable extent. The solubility of both investigated salts was determined by measuring the absorbance at 420 nm where $[\text{Fe}(\text{CN})_6]^{3-}$ has a maximum with the absorption coefficient $1\,035 \text{ mol}^{-1} \text{ kg cm}^{-1}$. At this wavelength, the absorbance of the complex cations is low, the absorption coefficients being 45 and $40 \text{ mol}^{-1} \text{ kg cm}^{-1}$ for $[\text{Cr}(\text{en})_3]^{3+}$ and $[\text{Cr}(\text{urea})_6]^{3+}$, respectively. These values were used for a correction when the molality of $[\text{Fe}(\text{CN})_6]^{3-}$ was calculated. The absorbances were measured on a SPECORD UV-VIS spectrophotometer (Zeiss, Jena).

RESULTS AND DISCUSSION

The solubilities of tris(ethylenediamine)chromium(III) and hexa(urea)chromium(III) hexacyanoferrates(III) in aqueous solutions of different supporting electrolytes and their standard deviations are reported in Table I and Table II. The experimental data are

TABLE I
Solubilities, S (mol kg^{-1}), and their standard deviations of $[\text{Cr}(\text{en})_3][\text{Fe}(\text{CN})_6]$ in aqueous solutions of supporting electrolytes of various molalities, m , at 25 °C

m	$S \cdot 10^4$	m	$S \cdot 10^4$	m	$S \cdot 10^4$
	NaClO ₄				(C ₂ H ₅) ₄ NBr
0	3.47 ± 0.06	0.030	23.5 ± 0.1	0.004	4.41 ± 0.20
0.004	4.21 ± 0.11	0.050	31.0 ± 0.3	0.010	6.28 ± 0.13
0.010	4.92 ± 0.19		KBr	0.030	8.85 ± 0.13
0.030	7.12 ± 0.22	0.004	4.06 ± 0.18	0.050	14.1 ± 0.3
0.050	8.26 ± 0.39	0.010	5.11 ± 0.33		(C ₃ H ₇) ₄ NBr
	Na ₂ SO ₄	0.030	7.43 ± 0.08	0.004	4.53 ± 0.07
0.004	6.95 ± 0.24	0.050	9.83 ± 0.10	0.010	6.27 ± 0.05
0.010	12.3 ± 0.4		(CH ₃) ₄ NBr	0.030	10.0 ± 0.1
0.030	23.1 ± 0.8	0.004	4.84 ± 0.22	0.050	14.0 ± 0.3
0.050	34.8 ± 0.8	0.010	5.75 ± 0.28		(C ₄ H ₉) ₄ NBr
	MgSO ₄	0.030	9.53 ± 0.07	0.004	4.84 ± 0.08
0.004	6.77 ± 0.32	0.050	16.0 ± 1.1	0.010	7.92 ± 0.26
0.010	10.9 ± 0.4			0.050	12.9 ± 0.5

averages from three independent measurements. It follows from Table I and Table II that the solubilities of the saturating salts increase with increasing ionic strength in all investigated solutions. For the dependence of the solubility on ionic strength, I , an empirical Güntelberg equation (I) was used.

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

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, $z_A z_B$. The dependence $\log (S/S_0) = f[\sqrt{I}/(1 + \sqrt{I})]$ was in all cases linear and enabled the extrapolation of the experimental values of S . The mean values of solubilities of the saturating salts, extrapolated to zero ionic strength, calculated from the data for all supporting electrolytes used, for $[\text{Cr}(\text{en})_3][\text{Fe}(\text{CN})_6]$ and $[\text{Cr}(\text{urea})_6][\text{Fe}(\text{CN})_6]$ were found to be $(2.11 \pm 0.07) \cdot 10^{-4} \text{ mol kg}^{-1}$ and $(3.85 \pm 0.08) \cdot 10^{-5} \text{ mol kg}^{-1}$, respectively. Using the extrapolated values the mean activity coefficients γ_{\pm} of the saturating salts were calculated as

$$\gamma_{\pm} = S_0/S \quad (2)$$

TABLE II
Solubilities, S (mol kg^{-1}), and their standard deviations of $[\text{Cr}(\text{urea})_6][\text{Fe}(\text{CN})_6]$ in aqueous solutions of supporting electrolytes of various molalities, m , at 25 °C

m	$S \cdot 10^4$	m	$S \cdot 10^4$	m	$S \cdot 10^4$
	NaClO ₄		Na ₂ SO ₄		KBr
0	0.45 ± 0.02	0.10	1.32 ± 0.01	0.050	2.33 ± 0.04
0.030	1.19 ± 0.03	0.020	1.98 ± 0.04	0.100	3.40 ± 0.02
0.060	1.80 ± 0.07	0.035	2.98 ± 0.07	0.150	4.20 ± 0.10
0.100	2.74 ± 0.08	0.050	3.48 ± 0.04	0.200	5.40 ± 0.13
0.200	5.12 ± 0.14				
	NaCl		MgSO ₄		(C ₄ H ₉) ₄ NBr
0.025	1.86 ± 0.06	0.010	1.52 ± 0.01	0.050	2.46 ± 0.21
0.050	2.38 ± 0.08	0.020	2.19 ± 0.02	0.075	3.44 ± 0.08
0.100	3.56 ± 0.18	0.030	2.76 ± 0.07	0.100	4.19 ± 0.13
0.200	4.89 ± 0.15	0.050	3.93 ± 0.13	0.150	5.69 ± 0.10

The increase in the solubility in Na_2SO_4 and MgSO_4 solutions can be related to the known ability of the sulfate ion to form ion pairs⁶. The abnormality low values of γ_{\pm} observed particularly for the more soluble ethylenediamine complex indicate, that the ions of the saturating salt are partially associated (cf. ref.⁶). With respect to the fact that the association influences predominantly the ionic strength, the small differences in solubilities observed in Na_2SO_4 and MgSO_4 solutions show that preferably ion pairs $[\text{Cr}(\text{en})_3]^+$, SO_4^{2-} exist in these solutions, the ion pairs $[\text{Cr}(\text{urea})_6]^{3+}$, SO_4^{2-} can be assumed as well. The experimental values of the mean activity coefficients can be satisfactorily reproduced by the semiempirical relation⁷

$$-\log \gamma_{\pm} = A |z_A z_B| \sqrt{I} / (1 + \sqrt{I}) - 0.1 |z_A z_B| I, \quad (3)$$

where $A = 0.509 \text{ mol}^{-1/2} \text{ kg}^{1/2}$ (25 °C in water), $|z_A z_B| = 9$. For the lowest ionic strength, corresponding to the saturated solutions of investigated complex salts, the calculated γ_{\pm} differ only 5% from their experimental values. The relationship (3) has been used also for the evaluation of the mean activity coefficients of the studied salts dissolved in water–organic mixed solvents.

The solubility data for water–cosolvent mixtures are reported in Table III. The solubility of $[\text{Cr}(\text{en})_3][\text{Fe}(\text{CN})_6]$ decreases with increasing concentration of the cosolvent, similar trend for $[\text{Cr}(\text{urea})_6][\text{Fe}(\text{CN})_6]$ has been observed only in the mixtures of water with *tert*-butyl alcohol. For the solutions of ethylenediamine complex the Eq. (4) is obeyed⁸

$$S_x = S_w \exp(-\lambda x), \quad (4)$$

where S_x and S_w are the solubilities of the salt in the mixture with mole fraction x of organic cosolvent and in water, respectively. The solvent precipitation constant λ for $[\text{Cr}(\text{en})_3][\text{Fe}(\text{CN})_6]$ has a value 4.6 in water–methanol and 14.7 in water–*tert*-butyl alcohol mixtures. The larger value of λ for *tert*-butyl alcohol solvent mixtures is evidently due to their lower relative permittivity as observed also in other systems⁹.

From the data given in Table III the Gibbs energies of transfer, ΔG_t^0 , of the investigated salts from water into the corresponding solvent mixtures were evaluated. According to the relationship between the Gibbs energies of solvation in water and in a mixed solvent, Eq. (5) can be written

$$\Delta G_t^0 = RT \ln (K_S^W / K_S^{\text{Mix}}). \quad (5)$$

K_S^W and K_S^{Mix} are the solubility products in water and in water-organic mixtures, respectively. Using the solubilities in these media, S^W and S^{Mix} , Eq. (6) is obtained for 1 : 1 electrolytes:

$$\Delta G_t^0 = 2RT \ln [(S^W/S^{Mix})(\gamma_{\pm}^W/\gamma_{\pm}^{Mix})] , \quad (6)$$

where γ_{\pm}^W and γ_{\pm}^{Mix} are the corresponding mean activity coefficients. They were calculated with the use of Eq. (3), the values of relative permittivities of investigated mixtures for the evaluation of Debye-Hückel constant A were taken from ref.¹⁰. The ΔG_t^0 values at various cosolvents concentrations are given in Table IV documenting that methanol destabilizes the solutions of tris(ethylenediamine) salt but has a stabilizing

TABLE III
Solubilities S (mol kg⁻¹), and their standard deviations for [Cr(en)₃][Fe(CN)₆] and [Cr(urea)₆][Fe(CN)₆] in water-cosolvent mixtures at 25 °C; w_{cos} (%) is weight fraction of cosolvent

w_{cos} , %	$S \cdot 10^4$	
	[Cr(en) ₃][Fe(CN) ₆]	[Cr(urea) ₆][Fe(CN) ₆]
CH ₃ OH		
10	2.26 ± 0.09	0.39 ± 0.09
20	1.69 ± 0.08	0.36 ± 0.03
30	1.06 ± 0.08	0.41 ± 0.01
40	0.87 ± 0.01	0.46 ± 0.04
<i>t</i> -C ₄ H ₉ OH		
10	2.48 ± 0.16	0.28 ± 0.01
20	1.68 ± 0.09	0.24 ± 0.01
30	0.94 ± 0.12	0.19 ± 0.01
40	0.48 ± 0.06	0.07 ± 0.00
CH ₃ CN		
10	7.16 ± 0.22	0.84 ± 0.08
20	9.32 ± 0.13	1.78 ± 0.01
30	8.08 ± 0.04	1.92 ± 0.08
40	4.36 ± 0.12	1.41 ± 0.08

effect on the solutions of hexaurea complex; *tert*-butyl alcohol destabilizes the solutions of both studied complex salts in contrast with the acetonitrile which has (with only one exception) a stabilizing effect on all solutions studied.

In order to evaluate the Gibbs energies of transfer of the ions of studied complexes the solubility of $[(\text{CH}_3)_4\text{N}]_3[\text{Fe}(\text{CN})_6]$ has been measured. The reason for the choice of this salt is that the Gibbs energies of transfer of $(\text{CH}_3)_4\text{N}^+$ ion from water into the mixtures of water with methanol¹¹ and *tert*-butyl alcohol¹² are known. However, only scarce data concerning the transfer of tetramethylammonium ion to water–acetonitrile mixtures have been published.

The Gibbs energies of transfer of $[\text{Cr}(\text{en})_3]^{3+}$ and $[\text{Cr}(\text{urea})_6]^{3+}$, $\Delta G_t^0(\text{Cr}^{3+})$, have been evaluated using Eq. (7). In this equation $\Delta G_t^0\{[\text{Cr}]^{3+}[\text{Fe}]^{3-}\}$ stands for the Gibbs energies of transfer of $[\text{Cr}(\text{en})_3][\text{Fe}(\text{CN})_6]$ and $[\text{Cr}(\text{urea})_6][\text{Fe}(\text{CN})_6]$, respectively.

$$\Delta G_t^0(\text{Cr}^{3+}) = \Delta G_t^0\{[\text{Cr}]^{3+}[\text{Fe}]^{3-}\} - \Delta G_t^0\{[(\text{CH}_3)_4\text{N}]_3[\text{Fe}(\text{CN})_6]\} + 3 \Delta G_t^0\{(\text{CH}_3)_4\text{N}^+\} \quad (7)$$

TABLE IV

Gibbs energies of transfer, ΔG_t^0 (kJ mol⁻¹), for $[\text{Cr}(\text{en})_3][\text{Fe}(\text{CN})_6]$ and $[\text{Cr}(\text{urea})_6][\text{Fe}(\text{CN})_6]$ from water to water–cosolvent mixtures at 25 °C (molality scale); w_{cos} (%) is weight fraction of cosolvent

w_{cos} , %	ΔG_t^0	
	$[\text{Cr}(\text{en})_3][\text{Fe}(\text{CN})_6]$	$[\text{Cr}(\text{urea})_6][\text{Fe}(\text{CN})_6]$
CH ₃ OH		
10	1.6 ± 0.2	-1.3 ± 1.1
20	3.0 ± 0.2	-1.0 ± 0.4
30	5.0 ± 0.4	-1.1 ± 0.1
40	6.1 ± 0.1	-1.5 ± 0.3
<i>t</i> -C ₄ H ₉ OH		
10	1.5 ± 0.3	0.3 ± 0.2
20	3.5 ± 0.3	1.3 ± 0.2
30	6.2 ± 0.6	2.5 ± 0.3
40	9.4 ± 0.6	7.1 ± 0.0
CH ₃ CN		
10	-2.5 ± 0.1	-4.6 ± 0.5
20	-2.8 ± 0.1	-7.4 ± 0.1
30	-1.8 ± 0.1	-7.4 ± 0.2
40	0.5 ± 0.1	-5.9 ± 0.3

All ionic transfer functions are based on TATB reference electrolyte assumption. It follows from the data in Table IV and Table V that the destabilization of the solutions of $[\text{Cr}(\text{en})_3][\text{Fe}(\text{CN})_6]$ with lower cosolvent concentrations is mainly due to the $[\text{Cr}(\text{en})_3]^{3+}$ cation. On the other hand, the solutions of $[\text{Cr}(\text{urea})_6][\text{Fe}(\text{CN})_6]$ with 10% of methanol are stabilized due to the negative Gibbs energy of transfer of $[\text{Fe}(\text{CN})_6]^{3-}$ anion. However, the stabilization of the solutions with higher methanol content is connected with the Gibbs energy of transfer of $(\text{Cr}(\text{urea})_6)^{3+}$ cation. The destabilization of the solutions of both studied complex salts in water-*tert*-butyl alcohol mixtures is evidently due to the considerable destabilization of the solutions of $[\text{Fe}(\text{CN})_6]^{3-}$ anion at 20, 30, and 40% of the cosolvent concentrations. The behaviour of both $[\text{Cr}(\text{en})_3]^{3+}$ and $[\text{Cr}(\text{urea})_6]^{3+}$ ions in water-*tert*-butyl alcohol mixtures is practically the same. The stabilization and/or destabilization of electrolyte solutions is determined by the solvation and preferential solvation of constituent ions in the mixed solvents. The differences observed in mixed solvents studied may be due to the different effect of the cosolvent on the cluster structure of water. *tert*-Butyl alcohol is known as a water-structure maker¹³, acetonitrile is a water-structure breaker¹⁴. Therefore in water-*tert*-butyl alcohol mixtures the number of free, non associated water molecules decreases with cosol-

TABLE V

Gibbs energies of transfer, ΔG_t^0 (kJ mol⁻¹) for $[(\text{CH}_3)_4\text{N}]_3[\text{Fe}(\text{CN})_6]$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Cr}(\text{en})_3]^{3+}$, and $[\text{Cr}(\text{urea})_6]^{3+}$ from water to water-cosolvent mixtures at 25 °C (molality scale); $w_{\text{cos}}(\%)$ is weight fraction of cosolvent

$w_{\text{cos}}, \%$	ΔG_t^0			
	$[(\text{CH}_3)_4\text{N}]_3[\text{Fe}(\text{CN})_6]$	$[\text{Fe}(\text{CN})_6]^{3-}$	$[\text{Cr}(\text{en})_3]^{3+}$	$[\text{Cr}(\text{urea})_6]^{3+}$
CH ₃ OH				
10	-4.2 ± 0.3	-6.8	8.4	5.5
20	3.0 ± 0.7	0.4	2.6	-1.4
30	6.3 ± 0.1	2.8	2.2	-3.9
40	5.1 ± 0.3	-0.3	6.4	-1.2
<i>t</i> -C ₄ H ₉ OH				
10	-1.7 ± 0.3	-3.5	5.0	3.8
20	7.8 ± 0.3	6.3	-2.8	-5.0
30	18.6 ± 0.8	22.8	-16.6	-20.3
40	27.6 ± 0.2	34.5	-25.1	-27.4

vent concentration. On the other hand, with increasing concentration of the acetonitrile the number of free water molecules increases. This interpretation leads to the conclusion that the acetonitrile in the mixtures with water enhances the hydration of the solute molecules and in this way stabilizes its solutions. *tert*-Butyl alcohol has mostly an opposite effect as can be seen in Table IV. The effect of methanol on the solutions of ethylenediamine complex salt differs from its effect on the solutions of hexaurea complex. According to data in Table IV the solutions of $[\text{Cr}(\text{en})_3][\text{Fe}(\text{CN})_6]$ are destabilized by the addition of methanol, whereas the corresponding solutions of $[\text{Cr}(\text{urea})_6][\text{Fe}(\text{CN})_6]$ are stabilized. It results from the data in Table V that the behaviour of methanol as a cosolvent is mainly due to its effect on the complex cations. The negative values of the Gibbs energy of transfer of $[\text{Cr}(\text{urea})_6]^{3+}$ at higher methanol concentrations indicates that the hydrogen bonds exist between the oxygen atom of the ligand and the molecules in the solvation shell.

REFERENCES

1. Arsuaga J. M., Castellanos M. A., Nunez-Delgado J.: *J. Chem. Thermodyn.* **14**, 555 (1982).
2. Arsuaga J. M., Caceres-Alonso M., Castellanos M. A., Nunez J.: *J. Solution Chem.* **18**, 379 (1989).
3. Holba V.: *Collect. Czech. Chem. Commun.* **57**, 2059 (1992); **58**, 1791 (1991); **59**, 1738 (1994).
4. Brauer G.: *Rukovodstvo po preparativnoi neorganicheskoi khimii*, p. 1603, 1606. Mir, Moskva 1985.
5. Stranks D. R.: *Modern Coordination Chemistry* (J. Lewis and R. G. Wilkins, Eds), p. 78. Interscience, New York 1960.
6. Davies C. W.: *Ion Association*, p. 105. Butterworths, London 1962.
7. Robinson R. A., Stokes R. H.: *Rastvory elektrolitov*, p. 264. Izdatel'stvo Inostrannoi Literatury, Moskva 1963.
8. Alfassi Z. B., Weiss J.: *Ber. Bunsenges. Phys. Chem.* **87**, 890 (1983).
9. Kacperska A.: *Phys. Chem. Liq.* **26**, 273 (1994).
10. Achadov Y. Y.: *Dielektricheskie svoistva binarnykh rastvorov*. Nauka, Moskva 1977.
11. Abraham M. H., Hill T., Ling H. C., Schulz R. A., Watt R. A. C.: *J. Chem. Soc., Faraday Trans.* **1** **80**, 489 (1984).
12. Talukdar H., Kundu K. K.: *J. Phys. Chem.* **96**, 970 (1992).
13. Koga Y., Sin W. W., Wong T. Y. H.: *J. Phys. Chem.* **94**, 7700 (1990).
14. Holba V.: *Collect. Czech. Chem. Commun.* **47**, 2484 (1982).