

SOLUBILITY AND THERMODYNAMIC TRANSFER FUNCTIONS OF CESIUM DIANILINETETRAISOTHIOCYANATOCHROMATE(III)

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The solubilities of cesium dianilinetetraisothiocyanatochromate(III) in water as well as in aqueous methanol, isopropyl alcohol, *tert*-butyl alcohol and acetonitrile were measured as a function of temperature and solvent composition. The Gibbs energies, enthalpies and entropies of transfer of the salt from water to the given solvents have been evaluated from experimental data. The contribution of $[\text{Cr}(\text{C}_6\text{H}_5\text{NH}_2)_2(\text{NCS})_4]^-$ ion to the Gibbs energy of transfer of the investigated salt has been calculated using the tetraphenylarsonium tetraphenylborate (TATB) reference electrolyte assumption.

Key words: Cesium salts; Chromium complexes; Solubility; Transfer functions.

The solutions of $[\text{Cr}(\text{C}_6\text{H}_5\text{NH}_2)_2(\text{NCS})_4]^-$ ion in water exhibit a strong absorption in the near ultraviolet region due to the NCS^- intraligand transition. The complex anion forms a salt with cesium cation. The salt is little soluble in water and in water-organic solvent mixtures. The low solubility of cesium dianilinetetraisothiocyanatochromate(III) makes it possible to use this salt for the extraction of cesium from water into organic solvents¹. The $[\text{Cr}(\text{C}_6\text{H}_5\text{NH}_2)_2(\text{NCS})_4]^-$ anion is also known as a precipitant of basic amino acids² and quaternary ammonium ions³. The data on the solubility of cesium salts with various anions are reported in ref.⁴. However, data on $\text{Cs}[\text{Cr}(\text{C}_6\text{H}_5\text{NH}_2)_2(\text{NCS})_4]$ are missing in the literature.

The aim of the present work was to gain experimental data on the solubility of cesium dianilinetetraisothiocyanatochromate(III) in water and in aqueous organic solvents at various temperatures and to evaluate the Gibbs energies, enthalpies and entropies of transfer of this salt from water to several binary solvent mixtures.

EXPERIMENTAL

Cesium dianilinetetraisothiocyanatochromate(III) was prepared by precipitation of a saturated solution of $\text{NH}_4[\text{Cr}(\text{C}_6\text{H}_5\text{NH}_2)_2(\text{NCS})_4] \cdot 1.5 \text{H}_2\text{O}$ prepared according to ref.⁵. Purity of the prepared salt was checked by elemental analysis and found satisfactory for this study. Methanol, isopropyl alcohol (Lachema, Brno, reagent grade), *tert*-butyl alcohol and acetonitrile (Merck, reagent grade) were distilled prior to use. Double distilled water was used in this work. Experimental technique involving ultrasonic agitation of samples in a jacked vessel kept at a desired temperature was as described in ref.⁶.

Absorbances of the solutions were measured on a Specord UV-VIS spectrophotometer (Carl Zeiss, Jena) at 307.7 nm (the molar absorption coefficient of the $[\text{Cr}(\text{C}_6\text{H}_5\text{NH}_2)_2(\text{NCS})_4]^-$, $\epsilon = 2.11 \cdot 10^4 \text{ kg mol}^{-1} \text{ cm}^{-1}$). Taking into consideration the standard error in the solubility determination, the average error in ΔG_{tr}^0 of the salt may be estimated $ca \pm 0.5 \text{ kJ mol}^{-1}$.

RESULTS AND DISCUSSION

The solubility of the investigated salt in aqueous organic solvents (at various concentrations of organic cosolvents) are summarized in Table I as a function of temperature.

TABLE I
Solubilities, $S \cdot 10^3$ (mol kg^{-1}), of $\text{Cs}[\text{Cr}(\text{C}_6\text{H}_5\text{NH}_2)_2(\text{NCS})_4]$ in water and in water-organic solvent mixtures of various composition and of various temperatures

Organic cosolvent wt. %	$T, ^\circ\text{C}$					
	17	25	30	35	40	45
0	0.57 ± 0.07	0.82 ± 0.08	1.09 ± 0.03	1.16 ± 0.04	1.31 ± 0.10	1.45 ± 0.01
	CH_3OH					
10	0.96 ± 0.03	1.09 ± 0.04	1.61 ± 0.08	1.90 ± 0.02	2.07 ± 0.06	2.50 ± 0.12
20	1.30 ± 0.05	1.83 ± 0.09	2.28 ± 0.03	2.86 ± 0.09	3.01 ± 0.07	3.35 ± 0.29
30	2.46 ± 0.08	3.04 ± 0.11	3.06 ± 0.03	4.29 ± 0.14	4.38 ± 0.02	5.23 ± 0.07
40	3.84 ± 0.32	5.56 ± 0.12	6.16 ± 0.50	6.92 ± 0.50	7.96 ± 0.08	8.25 ± 0.12
	$\text{iso-C}_3\text{H}_7\text{OH}$					
10	0.78 ± 0.01	0.81 ± 0.01	0.85 ± 0.02	1.82 ± 0.03	2.07 ± 0.05	2.40 ± 0.02
20	1.21 ± 0.06	2.13 ± 0.04	2.45 ± 0.02	3.62 ± 0.21	3.68 ± 0.12	4.17 ± 0.08
30	4.31 ± 0.10	5.21 ± 0.08	5.94 ± 0.05	7.52 ± 0.08	9.36 ± 0.11	11.1 ± 0.3
40	8.31 ± 0.31	9.84 ± 0.54	11.9 ± 0.2	14.0 ± 0.2	17.7 ± 0.5	18.6 ± 0.7
	$\text{tert-C}_4\text{H}_9\text{OH}$					
10	0.96 ± 0.04	1.03 ± 0.01	1.36 ± 0.04	1.52 ± 0.05	1.53 ± 0.05	1.67 ± 0.09
20	1.76 ± 0.03	2.46 ± 0.08	2.73 ± 0.10	2.80 ± 0.07	3.68 ± 0.12	4.22 ± 0.32
30	6.54 ± 0.27	8.22 ± 0.18	8.15 ± 0.31	9.36 ± 0.11	9.89 ± 0.20	10.2 ± 0.3
40	10.3 ± 0.2	11.4 ± 0.2	12.3 ± 0.1	14.6 ± 0.1	17.4 ± 0.8	17.9 ± 0.6
	CH_3CN					
10	0.86 ± 0.04	1.08 ± 0.04	1.18 ± 0.06	1.30 ± 0.02	1.52 ± 0.05	2.30 ± 0.09
20	1.36 ± 0.06	1.76 ± 0.12	1.90 ± 0.14	1.91 ± 0.04	2.65 ± 0.16	4.39 ± 0.16
30	5.47 ± 0.20	7.17 ± 0.51	9.35 ± 0.31	11.2 ± 0.6	16.6 ± 0.7	20.9 ± 0.5
40	–	8.44 ± 0.88	–	–	39.8 ± 1.9	–

The salt solubilities in water, S^w , and in binary solvent mixtures, S^{mix} , are related to the Gibbs energy of transfer of the salt, ΔG_{tr}^0 , by Eq. (1).

$$\Delta G_{\text{tr}}^0 = 2 RT \ln [(S^w/S^{\text{mix}})(\gamma_{\pm}^w/\gamma_{\pm}^{\text{mix}})] \quad (1)$$

Since the saturating salt is a 1 : 1 electrolyte and the ionic strength of saturated solutions is fairly low, the ratio of the mean activity coefficients, $\gamma_{\pm}^w/\gamma_{\pm}^{\text{mix}}$, is assumed to be unity. The ΔG_{tr}^0 values for different temperatures were fitted using Eq. (2).

$$\Delta G_{\text{tr}}^0 = a + bT + cT \ln T \quad (2)$$

With respect to the general relations $(\partial \Delta G / \partial T)_p = -\Delta S$ and $\Delta G = \Delta H - T\Delta S$, Eqs (3) and (4) hold for the enthalpy and the entropy of transfer.

$$\Delta H_{\text{tr}}^0 = a - cT \quad (3)$$

$$\Delta S_{\text{tr}}^0 = -b - c(1 + \ln T) \quad (4)$$

The results listed in Table I show that $\text{Cs}[\text{Cr}(\text{C}_6\text{H}_5\text{NH}_2)(\text{NCS})_4]$ is more soluble in aqueous organic solvent binary mixtures than in pure water. The values of the Gibbs energy, enthalpy and entropy of transfer for each solvent composition are listed in Table II. The reported data indicate that the investigated solutions are increasingly stabilized with increasing concentration of all the investigated organic cosolvents.

In order to evaluate the contributions of single ion to the Gibbs energy of transfer, the data for the transfer of Cs^+ ion from water to water–isopropyl alcohol and water–acetonitrile mixtures were taken from refs^{7,8}. For the Gibbs energy of transfer of $[\text{Cr}(\text{C}_6\text{H}_5\text{NH}_2)_2(\text{NCS})_4]^-$ ion, the following equation holds:

$$\Delta G_{\text{tr}}^0\{[\text{Cr}(\text{C}_6\text{H}_5\text{NH}_2)_2(\text{NCS})_4]^- \} = \Delta G_{\text{tr}}^0\{\text{Cs}[\text{Cr}(\text{C}_6\text{H}_5\text{NH}_2)_2(\text{NCS})_4]\} - \Delta G_{\text{tr}}^0(\text{Cs}^+). \quad (5)$$

The calculations of the single-ion transfer functions are based on the tetraphenylarsonium tetraphenylborate (TATB) reference electrolyte assumption. The values of the Gibbs energies of transfer of $[\text{Cr}(\text{C}_6\text{H}_5\text{NH}_2)_2(\text{NCS})_4]^-$ ion together with the earlier published data for water–methanol and water–*tert*-butyl alcohol mixtures³ are summarized

in Table III. It follows from the reported data as well as from the data published in ref.³ that the overall stabilization of the investigated solutions is due to the stabilization of the complex anion while cesium ion is destabilized in all the investigated solvents⁷⁻⁹. Measurements of the absorption spectra of the dianiline salt in the visible region showed that the d-d band at 550 nm did not shift when measured in the used aqueous organic solvents. This fact indicates that the steric configuration of the complex anion remains unchanged in these media. It is interesting to compare the Gibbs energies of transfer of the studied anion with the values of ΔG_{tr}^0 for the reineckate anion,

TABLE II
Thermodynamic functions of transfer of $\text{Cs}[\text{Cr}(\text{C}_6\text{H}_5\text{NH}_2)_2(\text{NCS})_4]$ from water to water-organic mixtures (molality scale, 298.1 K) and the coefficients in Eq. (2)

Organic cosolvent wt. %	ΔG_{tr}^0 kJ mol ⁻¹	ΔH_{tr}^0 kJ mol ⁻¹	$T\Delta S_{tr}^0$ kJ mol ⁻¹	a kJ mol ⁻¹	b kJ mol ⁻¹ K ⁻¹	c kJ mol ⁻¹ K ⁻¹
CH ₃ OH						
10	-1.9	-8.2	-6.3	-700.2182	15.5691	-2.3215
20	-3.9	-0.3	3.7	-140.3170	3.1336	-0.4697
30	-6.2	-26.0	-19.8	-945.0218	20.7134	-3.0828
40	-9.1	-12.0	-2.9	-203.3839	4.3088	-0.6419
iso-C ₃ H ₇ OH						
10	-0.2	-12.5	-12.3	-1 818.253	40.6103	-6.0574
20	-4.4	21.5	25.9	251.7858	-5.2604	0.7724
30	-9.0	-19.6	-10.6	-1 220.876	27.0252	-4.0299
40	-12.3	-18.6	-6.3	-906.7677	19.9748	-2.9793
tert-C ₄ H ₉ OH						
10	-1.5	-27.0	-25.5	-509.0816	10.9154	-1.6170
20	-4.9	-19.3	-14.4	-780.3464	17.1461	-2.5529
30	-11.0	-34.8	-23.7	-478.1792	10.0418	-1.4875
40	-12.9	-35.5	-22.6	-1 017.714	22.1422	-3.2948
CH ₃ CN						
10	-0.8	-32.1	-31.2	-1 583.140	34.9527	-5.2032
20	-3.0	-33.5	-30.5	-2 112.480	46.8112	-6.9741
30	-10.6	-1.3	9.4	-1 376.786	30.8721	-4.6142

$[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$. The data needed for the evaluation of ΔG_{tr}^0 for this ion have been taken from refs^{6,10,11}. With the increase in methanol concentration from 10 to 40 wt.% the Gibbs energy of transfer of the reineckate anion decreases from -2.2 to -6.9 kJ mol^{-1} , the corresponding data for water-*tert*-butyl alcohol mixtures are -1.4 to -8.3 kJ mol^{-1} . A comparison of these values with the data in Table III shows that $[\text{Cr}(\text{C}_6\text{H}_5\text{NH}_2)_2(\text{NCS})_4]^-$ ion is more stabilized in water-organic solvent mixtures than the $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ ion. It follows from Table II that the transfer process for the investigated salt is exothermic, $\Delta H_{\text{tr}}^0 < 0$, with only one exception for 20 wt.% of isopropyl alcohol. The dependences of ΔH_{tr}^0 on methanol, isopropyl alcohol and *tert*-butyl alcohol concentrations exhibit maxima at 20 wt.% of these cosolvents. The presence of such maxima in a water rich region can be attributed to the hydrophobic effect of the organic component (*cf.* ref.¹²). The role of a competition between organic cosolvent and the complex ion with organic coordination sphere cannot be excluded. Different behaviour of acetonitrile is probably due to the different binding of this cosolvent to the ions when compared with methanol and *tert*-butyl alcohol⁷. Strong dipole-dipole interactions with respect to the large dipole moment of acetonitrile¹³ may be also important. An alternative explanation is based on different effect of *tert*-butyl alcohol and acetonitrile on the cluster structure of water. The water structure-breaking effect of acetonitrile¹⁴ enhances the hydrophobic hydration, whereas the water structure-making *tert*-butyl alcohol has an opposite effect¹⁵. The tendency of acetonitrile to form hydrogen-bonded complexes with water as well as possible formation of dimers at higher acetonitrile concentrations (*cf.* ref.¹¹) bring further complications in the interpretation of the effect of this cosolvent on solubility and transfer functions of the investigated salt.

TABLE III

Gibbs energies of transfer, ΔG_{tr}^0 (kJ mol^{-1}), of $[\text{Cr}(\text{C}_6\text{H}_5\text{NH}_2)_2(\text{NCS})_4]^-$ ion from water to water-organic mixtures (molality scale, 298.1 K)

Cosolvent	Cosolvent concentration, wt.%			
	10	20	30	40
CH_3OH^a	-3.8	-5.5	-7.9	-11.4
iso- $\text{C}_3\text{H}_7\text{OH}$	-1.9	-7.9	-13.1	-
<i>tert</i> - $\text{C}_4\text{H}_9\text{OH}^a$	-4.3	-12.4	-15.6	-17.0
CH_3CN	-1.3	-3.6	-10.7	-

^a Data from ref.³.

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REFERENCES

1. Fujinaga T., Koyama M., Tochiyama O.: *J. Inorg. Nucl. Chem.* **1967**, 29, 1372.
2. Bergmann W.: *J. Biol. Chem.* **1935**, 110, 476.
3. Holba V.: *Collect. Czech. Chem. Commun.* **1994**, 59, 1738.
4. Fanning J. C.: *Coord. Chem. Rev.* **1995**, 140, 27.
5. Brauner G.: *Rukovodstvo po preparativnoi neorganicheskoi khimii*, p. 632. Izdatelstvo Inostrannoi Literatury, Moskva 1956.
6. Holba V.: *Chem. Papers* **1996**, 50, 253.
7. Benko J., Vollarova O., Cernusak I., Pappova A.: *J. Chem. Soc., Faraday Trans.* **1996**, 92, 4935.
8. Cox B. G., Natarajan R., Waghorne E.: *J. Chem. Soc., Faraday Trans. 1* **1979**, 75, 86.
9. Juillard J., Tissier C.: *Electrochim. Acta* **1982**, 27, 123.
10. Abraham M. H., Hill T., Ling H. C., Schulz R. A., Watt R. A. C.: *J. Chem. Soc., Faraday Trans. 1* **1984**, 80, 489.
11. Talukdar H., Kundu K. K.: *J. Phys. Chem.* **1992**, 96, 970.
12. Taniewska-Osinska S.: *Chem. Soc. Rev.* **1993**, 205.
13. Osipov O. A., Minkin V. I.: *Spravochnik po dipolnym momentam*. Vysshaya Shkola, Moskva 1965.
14. Holba V.: *Collect. Czech. Chem. Commun.* **1982**, 47, 2484.
15. Koga Y., Siu W. W. Y., Wong T. Y. H.: *J. Phys. Chem.* **1990**, 94, 7700.