

ACTIVITY COEFFICIENTS AND GIBBS ENERGIES OF TRANSFER OF TETRAALKYLAMMONIUM DIANILINETETRAISOTHIOCYANATOCHROMATES(III)

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The solubilities of tetraalkylammonium dianilinetetraisothiocyanatochromates(III) (alkyl = methyl, ethyl, 1-propyl, and 1-butyl) in water, water-methanol, water-*tert*-butyl alcohol and water-acetonitrile solutions were measured at 25 °C. The results were used to evaluate the activity coefficients and Gibbs energies of transfer of the saturating salts from water to the mixed systems. The Gibbs energies of transfer of the $[\text{Cr}(\text{C}_6\text{H}_5\text{NH}_2)_2(\text{NCS})_4]^-$ ion were obtained by means of known ionic transfer functions for the tetraalkylammonium ions based on the TATB assumption.

The complex dianilinetetraisothiocyanatochromate(III) anion, $[\text{Cr}(\text{C}_6\text{H}_5\text{NH}_2)_2(\text{NCS})_4]^-$, is known as a precipitant for basic amino acids¹ and has also been used for the extraction of cesium from water into nitrobenzene and nitropropane². Its concentrations in dilute solutions can be determined spectrophotometrically owing to its strong absorption in the near ultraviolet region due to the NCS^- intraligand transition.

With quaternary ammonium cations, the anion forms salts which are only sparingly soluble in water and in water-organic solvent mixtures. This property renders it possible to use solubility measurements for the evaluation of the activity coefficients as well as the thermodynamic transfer functions of the salts investigated. The limited kinetic stability of the complex anion³ requires a special experimental procedure, which has been described in relation to the investigation of tetraalkylammonium Reineckates⁴.

The aim of the present work was, from solubility data in water, to determine the mean activity coefficients of tetraalkylammonium dianilinetetraisothiocyanatochromates(III) and from measurements in water-organic solvent mixtures to evaluate the Gibbs energies of transfer of the salts and of the $[\text{Cr}(\text{C}_6\text{H}_5\text{NH}_2)_2(\text{NCS})_4]^-$ ion.

EXPERIMENTAL

Tetraalkylammonium dianilinetetraisothiocyanatochromates(III) were obtained by precipitation of a saturated solution of $\text{NH}_4[\text{Cr}(\text{C}_6\text{H}_5\text{NH}_2)_2(\text{NCS})_4]$. 1.5 H_2O (prepared following ref.⁵) with solutions of the tetraalkylammonium bromides (Merck, Darmstadt). The compounds prepared were checked by

elemental analysis using an Erba Science 1106 automatic analyzer (Milan). The results are given in Table I. Sodium perchlorate, methanol, and *tert*-butyl alcohol were products of Merck, Darmstadt (reagent grade) and were used as received, acetonitrile (Apolda, Germany) was distilled prior to use. All solutions were made by mass.

The measuring procedure involving ultrasonic agitation of the samples was as in ref.⁴. The concentrations of the saturating salts were determined spectrophotometrically. The absorbances were measured on a SPECORD UV-VIS spectrophotometer (Zeiss, Jena) at $32\,500\text{ cm}^{-1}$ (307.7 nm), where the extinction coefficient is $2.11 \cdot 10^4\text{ kg mol}^{-1}\text{ cm}^{-1}$.

RESULTS AND DISCUSSION

The solubilities S of the salts in aqueous solutions of sodium perchlorate are given in Table II. The measurements were performed at rather low ionic strengths where the relationship (1) for the dependence of solubility on ionic strength was satisfactorily fulfilled (a linear plot of $\log S$ vs $\sqrt{I}/(1 + \sqrt{I})$ was obtained):

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

For the present work it was important that with the aid of Eq. (1), the solubilities measured could be extrapolated to a zero ionic strength. Using the extrapolated values, S_0 , the mean activity coefficients γ_{\pm} were calculated as

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

TABLE I

Analytical data of tetraalkylammonium dianilinetetraisothiocyanatochromates(III), $R_4N[Cr(C_6H_5NH_2)_2(NCS)_4]$

R	Formula (M.w.)	Calculated/Found		
		% C	% H	% N
CH ₃	CrC ₂₀ H ₂₆ N ₇ S ₄ (544.5)	44.08	4.81	18.01
		44.20	4.84	18.22
C ₂ H ₅	CrC ₂₄ H ₃₄ N ₇ S ₄ (600.6)	47.96	5.71	16.33
		48.51	5.83	16.55
1-C ₃ H ₇	CrC ₂₈ H ₄₂ N ₇ S ₄ (656.6)	51.17	6.45	14.93
		50.76	6.53	14.68
1-C ₄ H ₉	CrC ₃₂ H ₅₀ N ₇ S ₄ (712.7)	53.87	7.07	13.76
		54.06	7.21	13.78

The experimental activity coefficients, reported in Table III for 0.1 and 0.5 mol kg⁻¹ NaClO₄ in water, can be compared with those evaluated by means of Eq. (3) (see ref.⁶), which are 0.7714 and 0.6896, respectively.

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

TABLE II

Solubilities S (mol kg⁻¹) and standard deviations of tetraalkylammonium dianilinetetraisothiocyanatochromates(III) in aqueous solutions of NaClO₄ of molality m (mol kg⁻¹) at 25 °C

m_{NaClO_4}	$S \cdot 10^5$	m_{NaClO_4}	$S \cdot 10^5$
Tetramethylammonium ^a		Tetraethylammonium ^b	
0	4.20 ± 0.07	0	5.15 ± 0.05
0.02	4.69 ± 0.04	0.01	5.60 ± 0.03
0.05	4.92 ± 0.06	0.02	5.63 ± 0.03
0.30	5.80 ± 0.08	0.10	6.25 ± 0.10
0.50	6.10 ± 0.15	0.30	6.92 ± 0.14
–	–	0.50	7.00 ± 0.02
Tetrapropylammonium ^c		Tetrabutylammonium ^d	
0	4.47 ± 0.14	0	2.30 ± 0.03
0.05	5.44 ± 0.10	0.01	2.52 ± 0.02
0.10	5.88 ± 0.16	0.02	2.57 ± 0.01
0.30	6.17 ± 0.26	0.10	2.87 ± 0.09
0.50	6.16 ± 0.05	0.20	3.17 ± 0.04
–	–	0.50	3.40 ± 0.03

All extrapolated values in mol kg⁻¹: ^a $S_0 = (4.173 \pm 0.011) \cdot 10^{-5}$; ^b $S_0 = (5.149 \pm 0.055) \cdot 10^{-5}$; ^c $S_0 = (4.572 \pm 0.075) \cdot 10^{-5}$; ^d $S_0 = (2.296 \pm 0.034) \cdot 10^{-5}$.

TABLE III

Experimental values of the mean activity coefficients γ_{\pm} of R₄N[Cr(C₆H₅NH₂)₂(NCS)₄] in aqueous solutions at two different concentrations of NaClO₄ at 25 °C

R	γ_{\pm} (0.1 m NaClO ₄)	γ_{\pm} (0.5 m NaClO ₄)
CH ₃	0.781	0.684
C ₂ H ₅	0.824	0.736
1-C ₃ H ₇	0.728	0.597
1-C ₄ H ₉	0.801	0.675

The agreement between the evaluated and experimental mean activity coefficients is best for the smallest cation, i.e. for $R = \text{CH}_3$, at both concentrations of NaClO_4 used. This is consistent with the theoretical conclusion that the non-electrostatic contribution to the activity coefficient value, which causes deviations from the Debye–Hückel law, occurs particularly in bulky ions⁷.

The solubility data for water–cosolvent mixtures reported in Table IV enable the evaluation of Gibbs energies of transfer, ΔG_t^0 , of the salts from water to the corresponding solvent mixtures. According to the relationship between the Gibbs energies of solvation in water and in a mixed solvent, in terms of the solubility products in these media K_S^W and K_S^{Mix} , respectively, Eq. (4) can be written in the form

$$\Delta G_t^0 = RT \ln (K_S^W/K_S^{\text{Mix}}) . \quad (4)$$

TABLE IV
Solubilities S (mol kg^{-1}) and their standard deviations for $\text{R}_4\text{N}[\text{Cr}(\text{C}_6\text{H}_5\text{NH}_2)_2(\text{NCS})_4]$ ($R = \text{CH}_3$, C_2H_5 , $1\text{-C}_3\text{H}_7$, $1\text{-C}_4\text{H}_9$) in water–cosolvent mixtures at 25 °C

Cosolvent wt. %	$S \cdot 10^4$			
	CH_3	C_2H_5	$1\text{-C}_3\text{H}_7$	$1\text{-C}_4\text{H}_9$
CH_3OH				
10	0.66 ± 0.01	0.86 ± 0.01	1.72 ± 0.07	0.54 ± 0.01
20	1.02 ± 0.01	1.58 ± 0.00	3.22 ± 0.04	1.25 ± 0.01
30	1.79 ± 0.01	3.28 ± 0.11	6.14 ± 0.09	3.34 ± 0.05
40	3.38 ± 0.12	8.15 ± 0.42	17.0 ± 0.9	10.3 ± 0.1
$t\text{-C}_4\text{H}_9\text{OH}$				
10	0.48 ± 0.01	0.67 ± 0.02	0.75 ± 0.02	0.38 ± 0.01
20	1.40 ± 0.04	2.03 ± 0.13	2.56 ± 0.12	1.37 ± 0.01
30	3.60 ± 0.05	5.61 ± 0.08	10.4 ± 0.2	2.75 ± 0.05
40	6.30 ± 0.20	10.1 ± 0.1	22.2 ± 0.2	15.5 ± 0.6
CH_3CN				
10	1.58 ± 0.04	2.38 ± 0.06	2.67 ± 0.09	0.13 ± 0.00
20	9.91 ± 0.55	14.7 ± 0.9	8.18 ± 0.47	2.56 ± 0.23
30	62.6 ± 4.7	78.7 ± 0.9	31.2 ± 0.9	13.8 ± 0.7

Using the solubilities in water and in the mixed solvent, S^W and S^{Mix} , Eq. (5) is obtained for 1 : 1 electrolytes:

$$\Delta G_t^0 = 2RT \ln [(S^W/S^{\text{Mix}}) (\gamma_{\pm}^W/\gamma_{\pm}^{\text{Mix}})] , \quad (5)$$

where γ_{\pm}^W , $\gamma_{\pm}^{\text{Mix}}$ are the corresponding activity coefficients. Their ratios were determined for $(\text{C}_2\text{H}_5)_4\text{N} \cdot [\text{Cr}(\text{C}_6\text{H}_5\text{NH}_2)_2(\text{NCS})_4]$ in water-*tert*-butyl alcohol mixtures. Their differences from unity were within the limits of experimental error. This was assumed to be true of all the other salts in all the solvent mixtures investigated. The ΔG_t^0 values at various cosolvent concentrations are given in Table V, documenting that with the exception of a single value in the last column, the organic cosolvents have a stabilizing effect on the solutions studied, and this effect increases with increasing cosolvent concentration (i.e. ΔG_t^0 becomes more negative). This behavior could be expected in view of the fact that both the cations and anions in the solutions contain hydrophobic groups. Appropriate extrathermodynamic assumptions are necessary for the evaluation of the

TABLE V

Gibbs energies of transfer of $\text{R}_4\text{N}[\text{Cr}(\text{C}_6\text{H}_5\text{NH}_2)_2(\text{NCS})_4]$ (R = CH₃, C₂H₅, 1-C₃H₇, 1-C₄H₉) from water to water-cosolvent mixtures at 25 °C (molality scale)

Cosolvent wt. %	ΔG_t^0 , kJ mol ⁻¹			
	CH ₃	C ₂ H ₅	1-C ₃ H ₇	1-C ₄ H ₉
	CH ₃ OH			
10	-2.23	-2.53	-6.67	-4.21
20	-4.42	-5.54	-9.79	-8.38
30	-7.18	-9.18	-12.9	-13.3
40	-10.3	-13.7	-18.8	-18.9
	<i>t</i> -C ₄ H ₉ OH			
10	-0.62	-1.31	-2.56	-2.45
20	-5.97	-6.79	-8.65	-8.83
30	-10.7	-11.8	-15.6	-12.3
40	-13.4	-14.7	-19.4	-20.9
	CH ₃ CN			
10	-6.58	-7.58	-8.86	2.90
20	-15.7	-16.6	-14.4	-11.9
30	-24.8	-24.9	-21.1	-20.3

Gibbs energies of transfer of the individual ions, ΔG_t^0 (R_4N^+) and ΔG_t^0 (complex ion⁻). The tetraphenylarsonium tetraphenylborate (TATB) reference electrolyte assumption⁸ is most frequently applied. A large volume of thermodynamic transfer function data based on the TATB assumption have been published for individual ions. For the evaluation of the Gibbs energy of transfer of the $[Cr(C_6H_5NH_2)_2(NCS)_4]^-$ anion from water to water-methanol mixtures, the experimental ΔG_t^0 values for the investigated salts were combined with transfer function data of tetraalkylammonium cations, $\Delta G_t^0\{R_4N^+\}$, from water to water-methanol and water-*tert*-butyl alcohol mixtures^{9,10} using Eq. (6):

$$\Delta G_t^0 \{ [Cr(C_6H_5NH_2)_2(NCS)_4]^- \} = \Delta G_t^0 - \Delta G_t^0 \{ R_4N^+ \} . \quad (6)$$

Only scarce data concerning the transfer of tetraalkylammonium ions to water-acetonitrile mixtures have been published. The Gibbs energies of transfer of the complex anion are given in Table VI. The data indicate that in both solvent mixtures used, the solutions of the complex anions are increasingly stabilized as the concentration of the organic cosolvent is increased. The stabilization is more pronounced in the water-*tert*-butyl alcohol mixtures than in the methanol-containing mixtures. It has been shown that the Gibbs energy of transfer of a hydrophobic ion comprises three contributions¹⁰ related to cavity formation, electrostatic interactions, and hydrophobic hydration, respectively. The hydrophobic hydration, requiring free water molecules, is strongly influenced by the structure-making character of *tert*-butyl alcohol¹¹ and by the structure-breaking

TABLE VI

Gibbs energies of transfer of dianilinetetraisothiocyanatochromates(III) anion, $\Delta G_t^0 \{ [Cr]^- \}$ (kJ mol⁻¹, molality scale) for the transfer from water to water-cosolvent mixtures at 25 °C

Cosolvent, wt. %	$\Delta G_t^0, \{ [Cr]^- \}$
CH ₃ OH	
10	-3.8
20	-5.5
30	-7.9
40	-11.4
<i>t</i> -C ₄ H ₉ OH	
10	-4.3
20	-12.4
30	-15.6
40	-17.0

properties of acetonitrile¹². However, as Table V demonstrates, cosolvents bring about stabilization of all solutions investigated (with only one exception) irrespective of their effect on the cluster structure of water. This indicates that in addition to the hydrophobic hydration, the electrostatic interactions, viz. ion–dipole, dipole–dipole, and dispersion interactions, play an important part in the solvation of the ions of the salts in water–organic cosolvents mixtures.

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