

Thermodynamic Functions of Transfer of Tetraalkylammonium Reineckates from Water to Water—Methanol and Water—*t*-Butyl Alcohol Mixtures

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The solubility of tetraalkylammonium diamminetetraisothiocyanato chromates(III) (alkyl = methyl, ethyl, 1-propyl, and 1-butyl) was measured in water and in water—methanol and water—*t*-butyl alcohol mixtures as a function of temperature and solvent composition. The results have been used to evaluate the Gibbs energy, enthalpy and entropy of transfer of the investigated salts from water to water—alcohol mixed solvents. The dependence of the thermodynamic transfer functions on concentration of organic cosolvents is discussed in terms of the cosolvent effect on the cluster structure of water.

Reinecke salt, *i.e.* ammonium diamminetetraisothiocyanato chromate(III) is known as a precipitant of various metal ions as well as amines, alkaloids, and some amino acids [1]. The quaternary ammonium salts, $R_4N[Cr(NH_3)_2(NCS)_4]$ ($R = CH_3, C_2H_5, 1-C_3H_7$, and $1-C_4H_9$), are only sparingly soluble in water and in water—alcohol solvent mixtures at lower organic cosolvents concentrations [2]. The complex anion $[Cr(NH_3)_2(NCS)_4]^-$ strongly absorbs in the near ultraviolet region because of the NCS^- intraligand transition, which enabled the determination of its concentration in the course of solubility measurements. The anion of the Reinecke salt is kinetically inert, nevertheless, its kinetic stability is limited with regard to the aquation, especially at higher temperatures [3]. With respect to this instability a special experimental technique has been used in the previous [2] as well as in the present work.

Solubility measurements of sparingly soluble salts in various solvents are often used in the evaluation of the thermodynamic transfer functions. The transfer from water as a reference solvent to aqueous-organic mixtures is of particular interest especially from the point of view of the effect of organic cosolvent on the cluster structure of water [4]. From the dependence of solubility on temperature the enthalpy and entropy of transfer can be evaluated [5, 6]. The tetraalkylammonium salts with various anions were studied in the past first of all because of their hydrophobic hydration and hydrophobic interactions [7]. It has been shown that the studied properties depend significantly on anion of the investigated salt. The study of transfer energetics of the sequence of the quaternary ammonium salts with a large complex anion provides further in-

formation on these interesting compounds. The aim of the solubility measurements in water—methanol and water—*t*-butyl alcohol mixed solvents was to gain the experimental data for the evaluation of the Gibbs energy, enthalpy and entropy of transfer from water to these media and to obtain the dependence of these quantities on concentration of the organic cosolvents.

EXPERIMENTAL

Tetraalkylammonium diamminetetraisothiocyanato chromates(III) have been prepared by precipitation of the saturated solution of $NH_4[Cr(NH_3)_2(NCS)_4]$ (Reinecke salt, USB Bruxelles, r.g.) with the solutions of tetraalkylammonium bromides (Lachema, Brno). The precipitates were washed with cold water and then dried in a desiccator over $CaCl_2$. The analytical data of the prepared compounds are summarized in Table 1. All other chemicals used were products of analytical purity (Merck, Darmstadt). Double distilled water was used throughout.

Measuring procedure. An excess of solid sample was added to approximately 25 cm³ of solvent in a jacketed vessel kept at a desired temperature by means of an ultrathermostat ($\pm 0.05^\circ C$) and plunged into the water bath of an ultrasound generator (UC 005, Tesla Vrable, Slovakia) with the output of 45 W at 38 kHz frequency. The duration of ultrasonic agitation, necessary for preparation of a saturated solution, was ascertained experimentally.

The evaluation of the concentration dependence of the saturating salt on duration of the sonication showed that no further changes took place after 360 s for all measured salts in all investigated media. Af-

Table 1. Characterization of the Prepared Compounds

Compound	M_r	$w_i(\text{calc.})/\%$ $w_i(\text{found})/\%$		
		C	H	N
$(\text{CH}_3)_4\text{N}[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$	392.4	24.46 23.92	4.61 4.60	24.98 25.10
$(\text{C}_2\text{H}_5)_4\text{N}[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$	448.5	32.11 31.77	5.83 5.88	21.86 22.10
$(1\text{-C}_3\text{H}_7)_4\text{N}[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$	504.6	38.05 38.10	6.79 7.00	19.43 19.81
$(1\text{-C}_4\text{H}_9)_4\text{N}[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$	560.6	42.81 42.61	7.55 7.65	17.49 17.34

ter attainment of equilibrium between the solid phase and its saturated solutions the system was filtered through a sintered glass and diluted, if necessary. The absorbance of solutions was measured by means of a spectrophotometer Specord UV VIS (Zeiss, Jena). The extinction coefficient of the Reineckate anion with the value of $16\,640\text{ kg mol}^{-1}\text{ cm}^{-1}$ at $\bar{\nu} = 33\,000\text{ cm}^{-1}$ ($\lambda = 303\text{ nm}$) was used for evaluation of the concentrations of the saturating salts. The standard deviation of the measured values of the solubility did not exceed 4 %.

RESULTS AND DISCUSSION

The solubility data of investigated salts in water as well as in water—methanol and water—*t*-butyl alcohol mixtures with various composition and various temperatures are summarized in Tables 2 and 3. The transfer of a salt from water to a mixed solvent is characterized by Gibbs energy of transfer, $\Delta_{\text{tr}}G^\circ$, given as a difference of the Gibbs energy of solvation of this salt in a mixed solvent, $\Delta_{\text{s}}G^\circ_{\text{mix}}$, and in water, $\Delta_{\text{s}}G^\circ_{\text{w}}$

$$\Delta_{\text{tr}}G^\circ = \Delta_{\text{s}}G^\circ_{\text{mix}} - \Delta_{\text{s}}G^\circ_{\text{w}} \quad (1)$$

With respect to the relation between the Gibbs energy of solution, $\Delta_{\text{sol}}G^\circ$ (the sum of the Gibbs energy of solvation and the crystal lattice energy of the salt), and the solubility product K_{S} , eqn (2) can be written for the Gibbs energy of transfer

$$\Delta_{\text{tr}}G^\circ = 2RT \ln[(S_{\text{w}}/S_{\text{mix}})(\gamma_{\pm\text{w}}/\gamma_{\pm\text{mix}})] \quad (2)$$

S_{w} and S_{mix} are the solubilities in water and in a mixed solvent, respectively, γ_{\pm} are the mean activity coefficients. Because all saturating salts investigated are 1:1 electrolytes and the ionic strength of the saturated solutions in all solvents used is low (not exceeding 0.003 mol dm^{-3}), the ratio of the activity coefficients was assumed to be one.

The $\Delta_{\text{tr}}G^\circ$ values calculated for different temperatures were fitted to eqn (3), the coefficients a, b, c were evaluated by the method of least squares.

$$\Delta_{\text{tr}}G^\circ = a + bT + cT \ln\{T\} \quad (3)$$

Table 2. Solubilities (S) for $\text{R}_4\text{N}[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, 1\text{-C}_3\text{H}_7, 1\text{-C}_4\text{H}_9$) in Water and in Water—Methanol Mixtures at Various Temperatures

θ °C	$S \cdot 10^4$ mol kg ⁻¹			
	CH ₃	C ₂ H ₅	1-C ₃ H ₇	1-C ₄ H ₉
	Water			
17	0.53	1.09	2.10	0.20
25	0.71	1.30	2.26	0.21
30	0.88	1.54	2.72	0.25
35	0.98	1.70	2.88	0.29
40	1.09	1.90	3.05	0.35
45	1.23	2.15	3.22	0.41
10 mass % CH ₃ OH				
17	0.99	1.76	2.70	0.35
25	1.02	1.87	3.24	0.38
30	1.06	2.03	3.65	0.45
35	1.11	2.24	4.75	0.67
40	1.18	2.51	6.51	1.02
45	1.27	2.84	8.93	1.48
20 mass % CH ₃ OH				
17	1.20	2.59	5.67	0.48
25	1.33	2.76	6.45	0.73
30	1.41	3.00	7.08	0.96
35	1.49	3.35	7.81	1.25
40	1.58	3.82	8.66	1.59
45	1.66	4.38	9.60	1.99
30 mass % CH ₃ OH				
17	1.58	3.75	8.86	1.29
25	1.61	4.03	11.3	1.30
30	1.77	4.36	12.6	1.59
35	2.07	4.79	13.6	2.11
40	2.54	5.33	14.3	2.83
45	3.15	5.98	14.8	3.77
40 mass % CH ₃ OH				
17	2.20	6.00	21.8	2.73
25	2.25	6.90	24.8	3.28
30	2.30	7.43	26.2	4.05
35	2.66	7.93	27.3	5.14
40	3.22	8.40	28.1	6.56
45	3.96	8.83	28.6	8.29

Table 3. Solubilities (S) for $R_4N[Cr(NH_3)_2(NCS)_4]$ ($R = CH_3, C_2H_5, 1-C_3H_7, 1-C_4H_9$) in Water— t -Butyl Alcohol Mixtures at Various Temperatures

θ °C	$S \cdot 10^4$ mol kg ⁻¹			
	CH ₃	C ₂ H ₅	1-C ₃ H ₇	1-C ₄ H ₉
10 mass % t -C ₄ H ₉ OH				
17	0.78	1.55	2.36	0.23
25	0.83	1.63	2.99	0.29
30	0.96	1.70	3.29	0.38
35	1.23	1.80	3.83	0.43
40	1.61	1.87	4.13	0.48
45	2.13	2.07	5.29	0.53
20 mass % t -C ₄ H ₉ OH				
17	1.08	2.38	4.04	0.62
25	1.25	2.50	5.95	0.64
30	1.45	2.65	6.93	0.82
35	1.78	3.12	7.57	1.15
40	2.89	4.03	7.97	1.60
45	4.43	5.66	8.29	2.19
30 mass % t -C ₄ H ₉ OH				
17	1.65	5.12	15.1	2.24
25	1.80	6.00	16.0	2.63
30	2.39	6.22	16.3	3.11
35	3.35	7.11	19.1	3.78
40	4.68	8.25	21.8	4.62
45	6.37	9.64	24.7	5.64
40 mass % t -C ₄ H ₉ OH				
17	4.35	9.79	28.1	3.95
25	4.46	11.0	30.5	4.54
30	5.18	11.9	32.2	5.52
35	6.40	13.1	34.1	6.94
40	8.10	14.5	36.8	8.81
45	10.3	16.0	40.7	11.1

With respect to the known relation, $(\partial \Delta G / \partial T)_p = -\Delta S$, and the relation $\Delta G = \Delta H - T\Delta S$, eqn (4) and eqn (5) hold for the enthalpy and the entropy of transfer

$$\Delta_{tr}H^\circ = a - cT \quad (4)$$

$$\Delta_{tr}S^\circ = -b - c(1 + \ln\{T\}) \quad (5)$$

Tables 2 and 3 show that the solubility of investigated salts with R_4N^+ cations passes through a maximum for $R = 1-C_3H_7$ and decreases sharply for $R = 1-C_4H_9$. Similar behaviour was observed for quaternary ammonium salts containing simple inorganic anions [7] as well as the complex anion $[Cr(C_6H_5NH_2)_2(NCS)_4]^-$ [8]. The values of Gibbs energy, $\Delta_{tr}G^\circ$, enthalpy, $\Delta_{tr}H^\circ$, and entropy of transfer, $T\Delta_{tr}S^\circ$ at 25°C evaluated for each solvent composition along with the values of coefficients a, b, c of eqn (2) are listed in Tables 4 and 5. The uncertainty of $\Delta_{tr}G^\circ$ values can be

estimated as $\pm 0.5 \text{ kJ mol}^{-1}$. It results from the reported data that for all investigated salts the Gibbs energy of transfer has negative values and decreases with increasing concentration of both methanol and t -butyl alcohol. The values of $\Delta_{tr}G^\circ$ indicate that the solutions of all salts studied are increasingly stabilized in the mixed solvents with increasing concentration of the organic cosolvent. The comparison of the Gibbs energies of transfer of the salts in the sequence from $R = CH_3$ to C_4H_9 shows that the stabilization is mainly due to the stabilization of quaternary ammonium cation (Tables 4 and 5). The use of tetraphenyl arsonium tetraphenyl borate (TATB) reference electrolyte assumption [9] enabled the evaluation of the Gibbs energy of transfer of Reinecke anion from water to water—methanol mixtures reported in [2]. The corresponding values are also negative, i.e. the $[Cr(NH_3)_2(NCS)_4]^-$ anion is stabilized, too, contributing to the overall stabilization of its salts with quaternary ammonium cations in water—organic solvent mixtures. Relatively simple dependence of the Gibbs energy of transfer on solvent composition for all salts investigated is not reflected in the enthalpies and entropies of transfer. Both these quantities change in a complicated way with cosolvents concentration passing through maxima and minima. Similar extrema have been observed in the past for the dependence of the enthalpies of transfer of quaternary ammonium ions from water to water— t -butyl alcohol mixtures [10–12]. A common feature of all obtained dependences is that these extrema occur in the range of small methanol and t -butyl alcohol concentrations similar to the enthalpic pair interaction coefficients observed in three-component systems electrolyte—water—alcohol [13]. Such extrema are generally taken to be associated with the effect of cosolvent on the cluster structure of water. t -Butyl alcohol is known as a water-structure maker, i.e. with increasing concentration of this cosolvent the number of monomeric, nonassociated water molecules decreases. This effect can influence the hydrophobic hydration which undoubtedly plays an important role in the investigated systems. On the basis of measurements of excess partial molar Gibbs energies and entropies in aqueous t -butyl alcohol solutions the existence of a characteristic boundary for the mole fraction of t -butyl alcohol, $x_B = 0.045$ (approx. 20 mass %) was demonstrated [14]. Below this boundary the alcohol enhances the water-structure, above it t -butyl alcohol molecules tend to form clusters. The detection of the boundary is consistent with earlier findings in the studies of water—organic solvent mixtures [15]. The data in Tables 4 and 5 show that the transfer of the investigated salts to water—alcohol mixtures leads to an increase of the entropy (with few exceptions). This behaviour is evidently associated with the hydrophobic hydration of ions of the salts. The water-structure making effect of alcohols results in less hydrophobic

Table 4. Thermodynamic Functions of Transfer of $R_4N[Cr(NH_3)_2(NCS)_4]$ ($R = CH_3, C_2H_5, 1-C_3H_7, 1-C_4H_9$) from Water to Water—Methanol Mixtures (Molality Scale, 25 °C) and the Coefficients a, b, c , of Eqn (3)

$w(t\text{-}CH_3OH)$	$\Delta_{tr}G^\circ$	$\Delta_{tr}H^\circ$	$T\Delta_{tr}S^\circ$	a	b	c
mass %	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	$\text{kJ mol}^{-1} \text{K}^{-1}$	$\text{kJ mol}^{-1} \text{K}^{-1}$
$R = CH_3$						
10	-1.3	-11	-9.8	245.1	-5.724	0.860
20	-2.6	-2.2	0.4	532.5	-12.01	1.794
30	-3.6	-1.0	2.7	-510.5	11.440	-1.709
40	-5.1	-7.8	-2.8	-547.3	12.130	-1.810
$R = C_2H_5$						
10	-1.5	-1.9	-0.9	4.084	-0.131	0.020
20	-2.4	-0.7	1.7	-72.95	1.615	-0.242
30	-5.3	-1.1	4.5	78.89	-1.810	0.268
40	-7.9	3.2	11	563.1	-12.62	1.878
$R = 1-C_3H_7$						
10	-1.7	-10	-8.5	-2030	45.42	-6.777
20	-4.8	8.9	14	13.25	-0.144	0.015
30	-7.5	19	27	642.7	-14.10	2.091
40	-11	2.2	13	412.0	-9.254	1.375
$R = 1-C_4H_9$						
10	-2.9	-1.1	1.8	1862	41.81	-6.243
20	-6.0	52	58	795.6	-16.22	2.393
30	-9.0	8.5	18	-708.9	16.06	-2.407
40	-13	23	36	53.23	-0.797	0.101

Table 5. Thermodynamic Functions of Transfer of $R_4N[Cr(NH_3)_2(NCS)_4]$ ($R = CH_3, C_2H_5, 1-C_3H_7, 1-C_4H_9$) from Water to Water—*t*-Butyl Alcohol Mixtures (Molality Scale, 25 °C) and the Coefficients a, b, c , of Eqn (3)

$w(t\text{-}C_4H_9OH)$	$\Delta_{tr}G^\circ$	$\Delta_{tr}H^\circ$	$T\Delta_{tr}S^\circ$	a	b	c
mass %	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	$\text{kJ mol}^{-1} \text{K}^{-1}$	$\text{kJ mol}^{-1} \text{K}^{-1}$
$R = CH_3$						
10	-0.3	2.0	2.4	-1183	26.62	-3.977
20	-1.4	11	12	-2102	47.44	-7.090
30	-4.3	33	37	-922.5	21.35	-3.206
40	-8.6	7.8	16	-753.1	17.04	-2.552
$R = C_2H_5$						
10	-1.0	-42	-41	-790.6	16.96	-2.512
20	-2.4	-32	-29	-2177	48.31	-7.198
30	-7.1	-14	-6.8	-631.2	13.89	-2.070
40	-10	-16	-5.4	-287.9	6.131	-0.913
$R = 1-C_3H_7$						
10	-0.6	19	19	-211.4	5.120	-0.774
20	-4.1	36	40	907.3	-19.69	2.920
30	-8.0	84	93	1807	-39.01	5.778
40	-12	-1.7	11	-208.1	4.599	-0.692
$R = 1-C_4H_9$						
10	-1.2	27	28	753.8	-16.43	2.439
20	-5.6	18	23	-801.6	18.33	-2.749
30	-12	15	27	160.3	-3.361	0.488
40	-15	17	32	-54.85	1.514	-0.242

hydration in the mixed solvents than in pure water, *i.e.* the lowering of the degree of organization takes place in the water—alcohol media.

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