

# Solubility and Thermodynamic Functions of Transfer for $[\text{Cr}(\text{en})_2\text{Cl}_2]$ $[\text{Cr}(\text{C}_6\text{H}_5\text{NH}_2)_2(\text{NCS})_4]$ from Water to Water-Organic Mixed Solvents

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The solubilities of *cis*- and *trans*-dichlorobis(ethylenediamine)chromium(III) salt of dianilinetetraisothiocyanatochromate(III) in water as well as in aqueous methanol, ethanol, propan-2-ol, 2-methylpropan-2-ol, acetonitrile, and ethylene carbonate were measured as a function of temperature and solvent composition. The Gibbs energies, enthalpies, and entropies of transfer of the saturating salts from water to the mixed solvents have been evaluated from solubility data. The contributions of *cis*- and *trans*- $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$  ions to the Gibbs energies of transfer of the investigated salts have been calculated using the tetraphenylarsonium tetraphenylborate reference electrolyte assumption.

The present paper is a continuation of our work on solubility and thermodynamic transfer functions of complex electrolytes which are composed of large ions [1]. Both investigated salts are only sparingly soluble in water in the temperature interval used, the addition of organic cosolvent increases their solubility. The complex anion absorbs strongly in the ultraviolet region due to the  $\text{NCS}^-$  intraligand transition, whereas the complex cation is practically transparent at the wavelengths where the  $[\text{Cr}(\text{C}_6\text{H}_5\text{NH}_2)_2(\text{NCS})_4]^-$  has an absorption maximum (Fig. 1). This enables the spectrophotometric determination of the concentration of saturating salts in the investigated solutions. The complex ions of the studied salts are of different kinetic stability with regard to the aquation, the most stable is the dianiline anion. Only few pieces of information exist on its aquation rate. Some data at an elevated temperature (70°C) can be found in [2]. The rate constants for the aquation of *cis*- and *trans*- $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$  ions are reported in [3]. With respect to the reduced kinetic stability of these ions an experimental technique based on ultrasonic agitation, described in [1], has been used.

The thermodynamic transfer functions of a sparingly soluble salt can be evaluated from solubility data in two different solvents, one of them, mostly water, is chosen as the reference one. The differences in the thermodynamic properties between the reference solvent and the solvent under study are then the thermodynamic transfer properties of the salt. The interpretation of experiments concerning the transfer to mixed aqueous solvents is more complicated as compared with the transfer into pure solvents. In the binary mixtures interactions of the ions of a saturat-

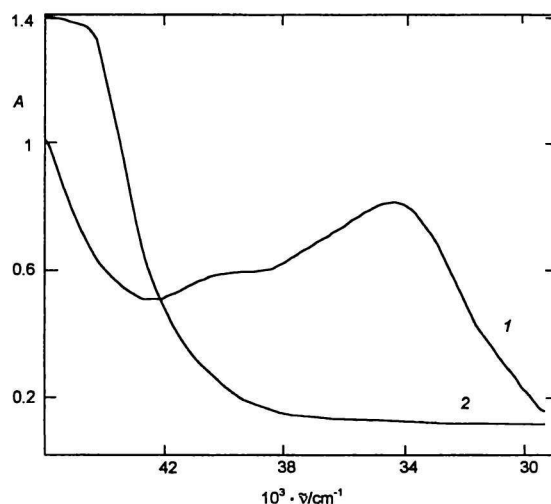


Fig. 1. Absorption spectra of complex salts. 1.  $4 \times 10^{-5}$  M- $\text{NH}_4[\text{Cr}(\text{C}_6\text{H}_5\text{NH}_2)_2(\text{NCS})_4]$ , 2.  $1 \times 10^{-3}$  M- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ . 1.00 cm path length.

ing salt with the mixture components as well as the solvent—solvent interactions must be involved. The properties of transfer into solvent mixtures include the preferential solvation of ions of the studied salt. In order to divide the transfer functions of a salt into the individual contributions of cation and anion several extrathermodynamic assumptions are employed. The most commonly applied assumptions for the Gibbs energy of transfer are tetraphenylarsonium tetraphenylborate (TATB) and tetraphenylphosphonium tetraphenylborate (TPTB) reference electrolyte assumptions [4, 5]. The thermodynamic transfer func-

tions of complex ions depend on composition of the coordination sphere. The large organic ligands render to the complex ions hydrophobic character and it is the reason of their stabilization by organic cosolvent.

The aim of the solubility measurements of the named salts in water and in aqueous organic mixtures at various temperatures was to obtain the experimental data for the evaluation of the Gibbs energy, enthalpy, and entropy of transfer from water to these media and to learn about the influence of organic cosolvents on the studied transfer properties.

## EXPERIMENTAL

The saturating salts, [*cis*-Cr(en)<sub>2</sub>Cl<sub>2</sub>][Cr(C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>)<sub>2</sub>(NCS)<sub>4</sub>] and [*trans*-Cr(en)<sub>2</sub>Cl<sub>2</sub>][Cr(C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>)<sub>2</sub>(NCS)<sub>4</sub>], were prepared by the precipitation of a saturated solution of NH<sub>4</sub>[Cr(C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>)<sub>2</sub>(NCS)<sub>4</sub>]·1.5H<sub>2</sub>O with saturated solutions of *cis*- and *trans*-[Cr(en)<sub>2</sub>Cl<sub>2</sub>]Cl, respectively. The dianiline chromate as well as both dichloro salts were prepared according to [6]. The precipitates were filtered, washed with cold water and dried in a desiccator over CaCl<sub>2</sub>. Purity of the prepared salts was checked by elemental analyses and by absorption spectra in visible and ultraviolet region. All organic cosolvents used were products of analytical purity (Merck, Darmstadt). Double distilled water was used throughout. Experimental technique of solubility measurements involving ultrasonic agitation of samples in a jacketed vessel kept at a desired temperature was as described in [1]. Absorbances of the saturated solutions after attaining equilibrium between the liquid and solid phases were measured on a Specord UV VIS spectrophotometer (Zeiss, Jena) at λ = 307.7 nm. The molar absorption coefficient of the [Cr(C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>)<sub>2</sub>(NCS)<sub>4</sub>]<sup>-</sup> ion with the value of 2.11 × 10<sup>4</sup> kg mol<sup>-1</sup>cm<sup>-1</sup> [7] was used for evaluation of the concentrations of the saturating salts. The effect of solvent on the absorption spectrum of the chromium(III) ion was thoroughly investigated by measuring the spectrum of solution of the chromium(III) complex salt successively in mixtures water—cosolvent (40 mass %) (methanol, isopropyl alcohol, *t*-butyl alcohol, acetonitrile). The position of maximum, its height and width did not differ measurably from the values in aqueous solution.

## RESULTS AND DISCUSSION

The solubilities of the investigated salts in aqueous organic solvents at various temperatures and concentrations of the organic cosolvents are summarized in Tables 1—3. The solubility data are means of 3—5 independent measurements. The solubility in water, *S<sub>w</sub>*, and in a binary solvent mixture, *S<sub>mix</sub>*, are related to the Gibbs energy of transfer of the saturating salt, Δ<sub>tr</sub>*G*<sup>o</sup> by eqn (1).

$$\Delta_{\text{tr}}G^{\circ} = 2RT \ln[(S_w/S_{\text{mix}})(\gamma_{\pm w}/\gamma_{\pm \text{mix}})] \quad (1)$$

Since the saturating salts are 1 : 1 electrolytes and the ionic strengths of saturated solutions are fairly low, the ratio of the mean activity coefficients, γ<sub>±w</sub>/γ<sub>±mix</sub>, is assumed to be unity. The Δ<sub>tr</sub>*G*<sup>o</sup> values calculated for different temperatures were fitted to eqn (2), the coefficients *a*, *b*, *c* were evaluated by the method of least squares.

$$\Delta_{\text{tr}}G^{\circ} = a + bT + cT \ln\{T\} \quad (2)$$

With respect to the general relations (∂Δ*G*/∂*T*)<sub>*p*</sub> = -Δ*S*, and Δ*G* = Δ*H* - *T*Δ*S* eqn (3) and eqn (4) hold for the enthalpy and the entropy of transfer.

$$\Delta_{\text{tr}}H^{\circ} = a - cT \quad (3)$$

$$\Delta_{\text{tr}}S^{\circ} = -b - c(1 + \ln\{T\}) \quad (4)$$

The values of Gibbs energy, Δ<sub>tr</sub>*G*<sup>o</sup>, enthalpy, Δ<sub>tr</sub>*H*<sup>o</sup>, and entropy of transfer, *T*Δ<sub>tr</sub>*S*<sup>o</sup> 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 Δ<sub>tr</sub>*G*<sup>o</sup> values can be estimated as ±0.5 kJ mol<sup>-1</sup>. The presented results show that both *cis* and *trans* isomers of [Cr(en)<sub>2</sub>Cl<sub>2</sub>][Cr(C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>)<sub>2</sub>(NCS)<sub>4</sub>] are more soluble in aqueous organic binary mixtures than in the pure water. There is only a little difference in solubility of *cis* and *trans* species. The negative values of the Gibbs energies of transfer in all investigated media indicate that the salts are increasingly stabilized in the mixed solvents with increasing concentration of the organic component. This stabilization is first of all due to the more hydrophobic complex anion which possesses large negative value of the Δ<sub>tr</sub>*G*<sup>o</sup> as shown in [7]. For the Gibbs energy of transfer of [Cr(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> ion the following equation holds

$$\begin{aligned} \Delta_{\text{tr}}G^{\circ}\{[\text{Cr}(\text{en})_2\text{Cl}_2]^+\} &= \Delta_{\text{tr}}G^{\circ}(\text{Salt}) - \\ &- \Delta_{\text{tr}}G^{\circ}\{[\text{Cr}(\text{C}_6\text{H}_5\text{NH}_2)_2(\text{NCS})_4]^{-}\} \end{aligned} \quad (5)$$

where Δ<sub>tr</sub>*G*<sup>o</sup>(Salt) is the Gibbs energy of transfer of [Cr(en)<sub>2</sub>Cl<sub>2</sub>][Cr(C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>)<sub>2</sub>(NCS)<sub>4</sub>]. Analogous equation holds for the enthalpy of transfer. The calculations of the single-ion transfer functions in the present work are based on tetraphenylarsonium tetraphenylborate (TATB) reference electrolyte assumption. The course of Δ<sub>tr</sub>*G*<sup>o</sup> for *cis*- and *trans*-[Cr(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> on going from water to water-organic mixtures is illustrated in Fig. 2. It follows from the presented data that the studied complex cations are destabilized in the aqueous mixtures of methanol, propan-2-ol, and 2-methylpropan-2-ol (*t*-butyl alcohol). In the mixtures of water with acetonitrile the

complex ions are stabilized. The solubility of [*trans*-Cr(en)<sub>2</sub>Cl<sub>2</sub>][Cr(C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>)<sub>2</sub>(NCS)<sub>4</sub>] is very similar to that of the *cis* isomer. The largest difference in the solubility of both isomers was observed in the mixtures with highest concentrations used of *t*-butyl alcohol. The Gibbs energies of transfer to these media

differ again only at highest cosolvent concentrations. However, the Gibbs energies of transfer have positive values for both complex ions, *i.e.* *cis*- and *trans*-[Cr(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> ions are destabilized in water—*t*-butyl alcohol mixtures. One possible explanation of the observed difference in the effect of *t*-butyl alcohol and

**Table 1.** Solubilities (*S*<sub>mix</sub>) for [*cis*-Cr(en)<sub>2</sub>Cl<sub>2</sub>][Cr(C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>)<sub>2</sub>(NCS)<sub>4</sub>] in Water–Organic Mixtures at Various Temperatures

$\theta / ^\circ\text{C}$	$w_1/\text{mass } \%$	$10^4 \cdot S_{\text{mix}}/(\text{mol kg}^{-1})$			
		10	20	30	40
CH <sub>3</sub> OH					
17	3.02 ± 0.02	4.24 ± 0.18	6.09 ± 0.09	14.0 ± 0.5	
25	3.57 ± 0.10	5.20 ± 0.06	9.47 ± 0.39	15.7 ± 0.1	
30	3.92 ± 0.14	5.78 ± 0.23	11.6 ± 0.3	17.7 ± 0.2	
35	4.27 ± 0.25	6.34 ± 0.23	13.8 ± 0.4	20.3 ± 0.6	
40	4.62 ± 0.15	6.88 ± 0.85	15.9 ± 0.4	23.6 ± 0.5	
45	4.98 ± 0.10	7.40 ± 0.12	18.1 ± 0.6	27.6 ± 0.2	
C <sub>2</sub> H <sub>5</sub> OH					
17	3.55 ± 0.12	5.57 ± 0.20	10.9 ± 0.5	26.6 ± 1.2	
25	4.44 ± 0.05	8.72 ± 0.11	16.7 ± 0.3	32.5 ± 0.2	
30	5.97 ± 0.19	11.5 ± 0.1	22.2 ± 0.8	41.8 ± 3.1	
35	8.25 ± 0.23	15.0 ± 0.1	29.3 ± 0.2	55.4 ± 1.0	
40	11.2 ± 0.3	19.1 ± 0.9	37.8 ± 1.0	73.2 ± 3.6	
45	15.0 ± 0.5	23.8 ± 0.4	47.8 ± 0.8	95.1 ± 2.1	
2-C <sub>3</sub> H <sub>7</sub> OH					
17	2.92 ± 0.02	4.19 ± 0.02	5.67 ± 0.21	13.9 ± 0.3	
25	3.85 ± 0.30	6.15 ± 0.08	11.2 ± 0.3	22.1 ± 1.2	
30	4.78 ± 0.04	8.08 ± 0.35	15.9 ± 0.1	30.0 ± 0.1	
35	5.97 ± 0.07	10.5 ± 0.1	21.8 ± 0.7	39.8 ± 0.2	
40	7.43 ± 0.21	13.5 ± 0.2	28.6 ± 0.4	51.7 ± 0.9	
45	9.14 ± 0.08	17.0 ± 0.2	36.4 ± 0.4	65.5 ± 2.2	
<i>t</i> -C <sub>4</sub> H <sub>9</sub> OH					
17	2.38 ± 0.02	5.25 ± 0.48	12.3 ± 0.4	17.6 ± 0.4	
25	3.17 ± 0.03	5.95 ± 0.16	12.4 ± 0.5	23.2 ± 1.4	
30	4.00 ± 0.17	7.57 ± 0.27	14.4 ± 0.4	27.0 ± 1.9	
35	5.07 ± 0.08	10.1 ± 0.1	17.8 ± 1.6	30.1 ± 2.1	
40	6.40 ± 0.08	13.5 ± 0.9	22.6 ± 0.1	35.2 ± 2.9	
45	7.98 ± 0.16	17.7 ± 0.3	28.8 ± 1.4	39.7 ± 1.9	
CH <sub>3</sub> CN					
17	4.70 ± 0.08	16.1 ± 0.2	66.1 ± 2.1	–	
25	6.92 ± 0.18	19.0 ± 0.6	89.2 ± 3.1	–	
30	7.89 ± 0.15	22.1 ± 0.4	103 ± 1	–	
35	8.55 ± 0.18	26.1 ± 1.0	116 ± 1	–	
40	8.89 ± 0.08	31.1 ± 1.6	129 ± 17	–	
45	8.93 ± 0.47	37.0 ± 0.2	141 ± 6	–	

**Table 2.** Solubilities (*S*<sub>i</sub>) for [*cis*-Cr(en)<sub>2</sub>Cl<sub>2</sub>][Cr(C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>)<sub>2</sub>(NCS)<sub>4</sub>] in Water and in Water–Ethylene Carbonate Mixtures at Various Temperatures

$\theta / ^\circ\text{C}$	$w_1/\text{mass } \%$	$10^4 \cdot S_i/(\text{mol kg}^{-1})$				
		0	5	10	15	20
17	1.64 ± 0.02	6.82 ± 0.12	10.2 ± 0.6	24.0 ± 0.8	38.8 ± 1.5	
25	2.65 ± 0.07	8.46 ± 0.41	13.8 ± 0.2	31.2 ± 3.8	40.5 ± 1.6	
30	2.86 ± 0.29	10.2 ± 0.2	17.7 ± 0.4	36.0 ± 1.5	44.2 ± 0.2	
35	3.36 ± 0.14	12.5 ± 0.6	23.0 ± 0.6	41.0 ± 1.1	55.5 ± 0.4	
40	3.84 ± 0.04	15.4 ± 0.4	29.5 ± 1.1	46.3 ± 1.7	71.7 ± 0.8	
45	4.18 ± 0.14	18.8 ± 0.3	37.4 ± 1.0	51.8 ± 0.8	92.9 ± 0.7	

**Table 3.** Solubilities ( $S_i$ ) for  $[trans-Cr(en)_2Cl_2][Cr(C_6H_5NH_2)_2(NCS)_4]$  in Water and in Water–*t*-Butyl Alcohol Mixtures at Various Temperatures

$\theta/^\circ C$	$10^4 \cdot S_i / (\text{mol kg}^{-1})$					
	$w_i/\text{mass \%}$	0	10	20	30	40
17		$1.77 \pm 0.02$	$2.37 \pm 0.10$	$3.03 \pm 0.04$	$12.2 \pm 0.1$	$23.8 \pm 0.5$
25		$2.22 \pm 0.08$	$2.83 \pm 0.24$	$6.64 \pm 0.04$	$21.8 \pm 0.2$	$32.2 \pm 0.2$
30		$2.55 \pm 0.24$	$3.43 \pm 0.24$	$9.16 \pm 0.01$	$28.0 \pm 0.2$	$38.4 \pm 0.3$
35		$2.91 \pm 0.08$	$4.27 \pm 0.05$	$11.9 \pm 0.05$	$34.3 \pm 0.2$	$45.4 \pm 0.9$
40		$3.29 \pm 0.08$	$5.34 \pm 0.09$	$14.8 \pm 0.5$	$40.8 \pm 0.2$	$53.2 \pm 0.2$
45		$3.71 \pm 0.06$	$6.65 \pm 0.05$	$17.9 \pm 0.2$	$47.4 \pm 0.5$	$61.7 \pm 0.6$

**Table 4.** Thermodynamic Functions of Transfer for  $[cis-Cr(en)_2Cl_2][Cr(C_6H_5NH_2)_2(NCS)_4]$  from Water to Water–Organic Mixtures (Molality Scale, 25°C) and the Coefficients  $a$ ,  $b$ ,  $c$  of Eqn (2)

$w_i$	$\Delta_{tr}G^\circ$	$\Delta_{tr}H^\circ$	$T\Delta_{tr}S^\circ$	$a$	$b$	$c$
mass %	$\text{kJ mol}^{-1}$	$\text{kJ mol}^{-1}$	$\text{kJ mol}^{-1}$	$\text{kJ mol}^{-1}$	$\text{kJ mol}^{-1} \text{K}^{-1}$	$\text{kJ mol}^{-1} \text{K}^{-1}$
CH <sub>3</sub> OH						
10	–1.8	–31.6	–29.8	–553.954	11.8360	–1.75234
20	–3.7	–28.3	–24.6	–518.953	11.1062	–1.64595
30	–6.6	8.2	14.8	–74.9239	1.81843	–0.27894
40	–9.2	–30.7	–21.5	–1064.13	23.2903	–3.46675
C <sub>2</sub> H <sub>5</sub> OH						
10	–3.2	5.5	8.7	–1431.58	32.2627	–4.821662
20	–6.3	21.7	28.0	–484.730	11.2762	–1.69749
30	–9.6	20.3	29.8	–633.799	14.5930	–2.19379
40	–13.0	–2.9	10.1	–1379.04	30.8837	–4.61633
2-C <sub>3</sub> H <sub>7</sub> OH						
10	–2.3	–2.3	0.03	–907.161	20.3199	–3.03372
20	–4.6	9.4	13.9	–710.426	16.2332	–2.43365
30	–7.5	51.9	59.3	39.920	0.07460	–0.07460
40	–11.0	20.7	31.6	–760.845	17.4528	–2.62172
<i>t</i> -C <sub>4</sub> H <sub>9</sub> OH						
10	–1.3	–2.1	–0.9	–931.211	20.9314	–3.63481
20	–4.6	–10.4	–5.8	–1655.10	36.9708	–5.51725
30	–7.9	–32.6	–24.4	–2653.72	58.8812	–8.77687
40	–11.1	–12.9	–1.8	–484.642	10.5896	–1.57984
CH <sub>3</sub> CN						
10	–5.0	–7.7	–2.7	343.946	–7.90568	1.18212
20	–10.2	–27.0	–17.3	–1046.29	23.0470	–3.43512
30	–17.4	–13.2	–4.6	–275.044	5.86889	–0.87861
Ethylene Carbonate						
5	–6.2	–11.6	–5.4	–1024.34	22.5117	–3.35862
10	–8.6	1.7	10.3	–1119.89	25.1635	–3.76234
15	–12.6	–17.0	–4.5	–526.870	11.4697	–1.71031
20	–13.8	–36.9	–23.2	–2025.27	44.7496	–6.66998

**Table 5.** Thermodynamic Functions of Transfer for  $[trans-Cr(en)_2Cl_2][Cr(C_6H_5NH_2)_2(NCS)_4]$  from Water to Water–*t*-Butyl Alcohol Mixtures (Molality Scale, 25°C) and the Coefficients  $a$ ,  $b$ ,  $c$  of Eqn (2)

$w_i$	$\Delta_{tr}G^\circ$	$\Delta_{tr}H^\circ$	$T\Delta_{tr}S^\circ$	$a$	$b$	$c$
mass %	$\text{kJ mol}^{-1}$	$\text{kJ mol}^{-1}$	$\text{kJ mol}^{-1}$	$\text{kJ mol}^{-1}$	$\text{kJ mol}^{-1} \text{K}^{-1}$	$\text{kJ mol}^{-1} \text{K}^{-1}$
10	–1.7	–26.7	–25.0	–1523.50	33.7123	–5.02109
20	–5.2	75.3	80.5	1176.20	–25.0049	3.69318
30	–11.2	46.5	57.7	804.664	–17.2277	2.54339
40	–13.2	12.2	25.4	51.7071	–0.97339	0.13260

acetonitrile on transfer properties is based on different effect of these cosolvents on cluster structure of water. *t*-Butyl alcohol is known as a water-structure maker, *i.e.* with its increasing concentration in an aqueous mixture the number of monomeric, nonassociated water molecules decreases [8]. However, at higher mass fractions (> 20 mass %) *t*-butyl alcohol tends to form clusters. This property is evidently responsible for lowering of the destabilizing effect at higher concentrations of this cosolvent. On the other hand, acetonitrile is water-structure breaker, the number of free water molecules increases with its increasing concentration in a binary aqueous mixture [9]. The described properties of named cosolvents are closely related to the concept of hydrophobic hydration which is enhanced by water-structure breaking compounds. The maxima on the dependence  $\Delta_{tr}G^{\circ}$  (ion) *vs.* cosolvent concentration for other alcohols used can also be related to the existence of a characteristic boundary for these cosolvents in their mixtures with water [10]. Another interpretation of the properties of transfer of ions into pure solvents as well as solvent mixtures on a molecular level uses the conception of coordinative interactions of ions with solvent molecules [11]. For this purpose solvents are classified as molecules with hard donor atoms (*e.g.* O) and soft donor atoms (*e.g.* N, S) in a sense of the concept of hard and soft acids and bases [12, 13]. A different coordination behaviour of solvents *vs.* ionic solutes is reflected in the Gibbs energies of transfer. The differences in the course of the dependence of  $\Delta_{tr}G^{\circ}$  on alcohol concentration on one side and on acetonitrile concentration on the other can be well understood using the idea of ion—solvent coordinative interactions.

Only few data exist on single-ion transfer enthalpies which are indispensable for the evaluation of the enthalpies of transfer for *cis*- and *trans*-[Cr(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>. They were evaluated using the data taken from [14]. The behaviour of  $\Delta_{tr}H^{\circ}$  on going from water to water—*t*-butyl alcohol mixtures is illustrated in Fig. 3. A striking difference between both isomers can be seen in this figure. This fact is again in harmony with the conception of ion—solvent coordinative interactions which are more stereospecific than interactions governed by electrostatic forces alone.

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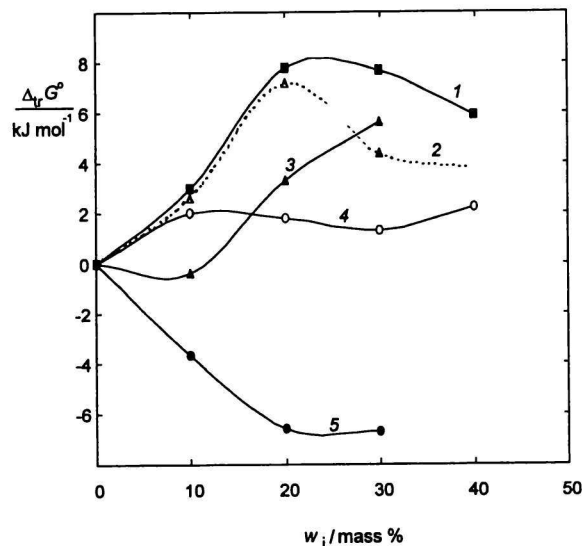


Fig. 2. Gibbs energies of transfer,  $\Delta_{tr}G^{\circ}$ , to water-organic mixtures at 25°C for *cis*-[Cr(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> (full lines) and *trans*-[Cr(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> (dashed line). 1, 2. *t*-C<sub>4</sub>H<sub>9</sub>OH, 3. 2-C<sub>3</sub>H<sub>7</sub>OH, 4. CH<sub>3</sub>OH, 5. CH<sub>3</sub>CN.

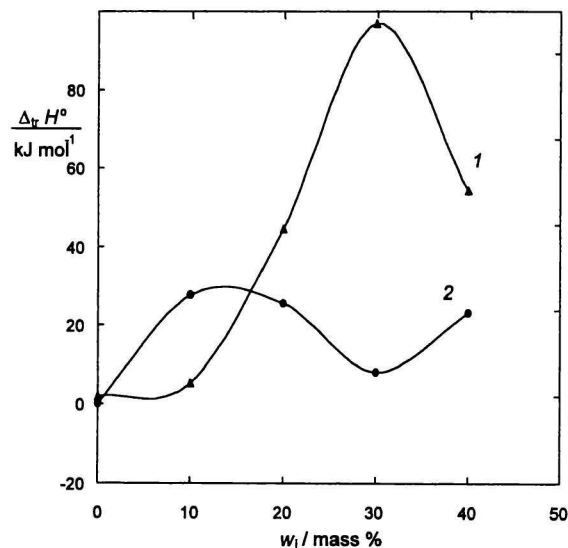


Fig. 3. Enthalpies of transfer,  $\Delta_{tr}H^{\circ}$ , to water—*t*-butyl alcohol mixtures. 1. *cis*-[Cr(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>, 2. *trans*-[Cr(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>

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