

TRANSFER THERMODYNAMIC FUNCTIONS ΔG_t^0 , ΔH_t^0 AND $T\Delta S_t^0$ OF *cis*- AND *trans*-[CoCl₂(en)₂]⁺ ISOMERS IN AQUEOUS MIXTURES OF METHANOL, *tert*-BUTYL ALCOHOL AND ACETONITRILEOl'ga VOLLÁROVÁ^{1,*} and Ján BENKO²

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Dedicated to Professor Eudovít Treindl on the occasion of his 70th birthday.

The solubility, partial molar volume and standard integral molar enthalpy of solution of *cis*- and *trans*-[CoCl₂(en)₂]Cl in water, aqueous methanol, aqueous *tert*-butyl alcohol and aqueous acetonitrile are reported. The transfer functions ΔG_t^0 , ΔH_t^0 and $T\Delta S_t^0$ as well as partial molar volumes are used to obtain information on the solute-solvent interactions. Results obtained are discussed in terms of differences in the surface charge distribution in isomeric coordination species.

Key words: Complex ions; Solvation; Transfer thermodynamic functions; Partial molar volumes; Thermodynamics; Cobalt; Solubility.

Ion transfer properties such as Gibbs energies, enthalpies, entropies of transfer and partial molar volumes have been found to be a valuable means in understanding the interactions of solvent molecules with ions¹. Data in terms of ΔG_t^0 can be obtained from solubility, ΔH_t^0 data may be obtained calorimetrically, by measuring enthalpy of solution, ΔS_t^0 values are derived from appropriate enthalpies and Gibbs energies and partial molar volumes can be calculated from density of solutions. Much work has been done on transfer Gibbs energies of variety of transition metal complexes^{2,3} but only a little attention has been paid to transfer enthalpies and entropies of complex ions⁴. Our interest in the transfer thermodynamic function of *cis*- and *trans*-[CoCl₂(en)₂]⁺ in various aqueous mixtures of methanol, *tert*-butyl alcohol and acetonitrile arises for several reasons. The chosen complex compounds are easily prepared as a good soluble chloride salts (suitable for enthalpies of solution measurements) and as a less soluble perchlorate salts (low solubility is favourable for ΔG_t^0 determination) and they are suffi-

ciently stable both in the solid state and in solution. The solubilities, enthalpies of solution and partial molar volumes of both isomers have not been published yet, except of solubilities of *trans*-[CoCl₂(en)₂]ClO₄ in water and water-methanol mixtures⁵. The chosen organic cosolvents differ in their hydrophobic/hydrophilic character and have the dipole moments from 1.66 to 3.92 D. The transfer functions ΔG_t^0 , ΔH_t^0 and $T\Delta S_t^0$ as well as partial molar volumes are used to obtain the information about the role of charge distribution on the surface of complex ion in solute-solvent interaction.

EXPERIMENTAL

Materials

Cis and *trans* isomers of [CoCl₂(en)₂]Cl as well as of [CoCl₂(en)₂]ClO₄ were prepared by the literature method⁶. Their purity was checked by elemental analysis and their electronic absorption spectra. All solvents were redistilled before use.

Measurements

Solubility. Concentration of a complex in the equilibrium saturated solution was determined using a spectrophotometer Specol 210 and wavelength 527 and 625 nm for *cis* and *trans* isomer, respectively. An ultrasonic generator Tesla UC 005 AJ1 with the output of 30 W at 50 kHz frequency was used to speed up attainment of equilibrium (ultrasonic agitation did not exceed 10 min) to prevent aquation and/or isomerisation of cobalt species. The standard error in the solubility value was up to 3%.

Standard integral molar enthalpy of solution, ΔH_s^0 , was measured using an isoperibolic calorimeter constructed at Technical University Brno (Czech Republic) as described earlier⁷. The experimental data are averages of four independent measurements. The standard deviations of the ΔH_s^0 measured did not exceed ± 0.7 kJ mol⁻¹.

Partial molar volumes. Density of Co(III) complex solutions at 298.15 ± 0.01 K was measured by using an Anton Paar DMA60/602 digital vibrating densimeter calibrated with water⁸ ($\rho = 0.997045$ g cm⁻³) and nonane⁹ ($\rho = 0.713850$ g cm⁻³). The uncertainty in density values was ± 0.00001 g cm⁻³. The temperature was regulated by a cascade water bath apparatus (Heto) stable within ± 0.01 K and checked with a digital thermometer (Anton Paar DT 100-20). Measurements were made at 5 mmol dm⁻³ concentration of the Co(III) complex. Values of the apparent partial molar volume, V^0 , were calculated from densities. The V^0 values were independent of concentration within the experimental error, so they were taken as standard values. The standard error in the partial molar volume was determined from 3-5 independent measurements and did not exceed ± 3.0 cm³ mol⁻¹.

RESULTS AND DISCUSSION

The solubility of salts in water, S_w , and in solvent mixtures, S_{x_2} , are related to the standard transfer Gibbs energy, ΔG_t^0 , of the salt by

$$\Delta G_t^0 = 2RT \ln \frac{S_w \gamma_w^\pm}{S_{x_2} \gamma_{x_2}^\pm} \quad (1)$$

where γ_w and γ_{x_2} are mean molar activity coefficients of salt. With regard to the relatively low solubility (Table I) the γ_w/γ_{x_2} can be approximated by unity. Transfer Gibbs energy of complex cations (Table II) can be calculated using published estimates for the ClO₄⁻ ion in aqueous mixtures of MeOH (ref.¹⁰), *t*-BuOH (ref.¹¹) and AN (ref.¹¹).

$$\Delta G_t^0 [\text{Co(en)}_2\text{Cl}_2]^+ = \Delta G_t^0 [\text{Co(en)}_2\text{Cl}_2]\text{ClO}_4 - \Delta G_t^0 [\text{ClO}_4]^- \quad (2)$$

Values of the standard transfer enthalpy of solution, ΔH_t^0 , were calculated by using Eq. (3)

$$\Delta H_t^0 (\text{salt}) = \Delta H_s^0 (x_2) - \Delta H_s^0 (w) \quad (3)$$

where $\Delta H_s^0 (x_2)$ and $\Delta H_s^0 (w)$ are enthalpies of solution in aqueous solvent and water, respectively. Values of the transfer enthalpy of solution of complex cations (Table II) were calculated using published data for $\Delta H_t^0 (\text{Cl}^-)$ in aqueous mixtures of MeOH (ref.¹⁰), *t*-BuOH (ref.¹²) and MeCN (ref.¹³). All the ionic transfer functions listed in Table II are based on the TATB or TPTB extrathermodynamic assumption, i.e., $\Delta G_t^0 (\text{Ph}_4\text{As}^+)$ or $\Delta G_t^0 (\text{Ph}_4\text{P}^+) = \Delta G_t^0 (\text{Ph}_4\text{B}^-)$ (Ph_4As^+ , tetraphenylarsonium; Ph_4P^+ , tetraphenylphosphonium; Ph_4B^- , tetraphenylborate)¹⁴.

Solubility data for *trans*-[CoCl₂(en)₂]ClO₄ in water–MeOH mixtures presented in Table I are in good agreement with the literature data⁵. The solubility change with increasing mole fraction of organic cosolvent (Table I) shows a significant participation of the solvent effects in the dissolution of investigated complexes. The change in solubility is due to change in solvent structure¹⁵. The opposite trend of solubility in aqueous mixture of alcohols and acetonitrile (Table I) is due to the effect of cosolvent on water structure. In aqueous mixtures of alcohols, where the enhancement of the water structure near the hydrophobic groups could be expected, the solubility decreases with mole fraction of organic cosolvent. Unlike the alcohols, dipolar aprotic acetonitrile is hydrophilic and has the ability to break the structure of water. The differences in ΔG_t^0 vs mole fraction of organic cosolvent, for both ionic isomers in Table II are smaller than their experi-

TABLE I

Dependences of the solubilities, S , partial molar volumes, V^0 , of *cis* and *trans* isomers of $[\text{CoCl}_2(\text{en})_2]\text{ClO}_4$ and standard integral molar enthalpies of solution, ΔH_s^0 , of *cis* and *trans* isomers of $[\text{CoCl}_2(\text{en})_2]\text{Cl}$ on the mole fraction of organic cosolvent, x_2 , at 298.2 K

x_2	<i>cis</i> Isomer			<i>trans</i> Isomer		
	$S \cdot 10^2$ mol dm ⁻³	V^0 cm ³ mol ⁻¹	ΔH_s^0 kJ mol ⁻¹	$S \cdot 10^2$ mol dm ⁻³	V^0 cm ³ mol ⁻¹	ΔH_s^0 kJ mol ⁻¹
0	6.34	171.2	30.1	1.32 1.30 ^a	184.0	19.0
<i>tert</i> -Butyl alcohol						
0.010	6.36	173.7	32.8	1.23	192.5	19.3
0.021	6.37	161.2	35.0	1.14	173.1	21.3
0.033	4.66	155.2	37.4	1.11	165.2	24.5
0.046	4.27	152.0	39.6	1.04	163.2	28.7
0.076	4.49	137.6	41.2	0.98	161.5	30.2
0.113	3.92	135.5	38.9	0.92	157.1	28.8
Acetonitrile						
0.017	6.26	171.7	32.5	1.47	182.4	17.7
0.036	6.50	168.7	31.4	1.69	193.7	17.5
0.057	6.92	168.0	31.1	1.98	186.3	16.5
0.077	8.58	160.3	30.0	2.37	171.5	15.8
0.126	11.45	141.2	25.7	3.24	144.6	14.5
0.182	14.6	126.3	25.5	4.12	120.8	13.8
Methanol						
0.047	5.09	–	32.1	1.19	–	21.2
0.100	4.27	–	32.8	1.14 1.09 ^a	–	22.9
0.160	3.83	–	34.5	1.05	–	23.9
0.229	3.39	–	33.7	1.02 0.9 ^a	–	23.7
0.309	3.12	–	32.7	0.97	–	21.6

^a Values taken from ref.⁵

TABLE II
Dependence of the transfer enthalpies, ΔH_t^0 , transfer Gibbs energies, ΔG_t^0 , and transfer entropies, $T\Delta S_t^0$, of *cis* and *trans* isomers of [CoCl₂(en)₂]⁺ ions on the mole fraction of organic cosolvent, x_2 , at 298.2 K

x_2	<i>cis</i> Isomer			<i>trans</i> Isomer		
	ΔH_t^0 kJ mol ⁻¹	ΔG_t^0 kJ mol ⁻¹	$T\Delta S_t^0$ kJ mol ⁻¹	ΔH_t^0 kJ mol ⁻¹	ΔG_t^0 kJ mol ⁻¹	$T\Delta S_t^0$ kJ mol ⁻¹
<i>tert</i> -Butyl alcohol						
0.010	3.8	-0.2	4.0	0.4	0.4	0.0
0.021	4.9	0.3	4.6	2.3	1.0	1.3
0.033	10.0	1.6	8.4	8.2	0.8	7.4
0.046	17.6	1.4	16.2	17.8	0.6	17.2
0.076	13.5	-0.4	13.9	13.6	-0.7	14.3
0.113	5.1	-0.9	6.0	6.0	-1.7	7.7
Acetonitrile						
0.017	3.3	0.5	2.8	0.2	-0.2	0.0
0.036	2.8	0.5	2.3	0.0	-0.5	0.5
0.057	3.0	1.1	1.9	-0.5	-0.5	0.0
0.077	1.2	0.8	0.4	-2.1	-0.7	-1.4
0.126	-9.3	-0.5	-8.8	-9.5	-2.3	-7.2
0.182	-14.9	-1.9	-12.0	-15.5	-3.4	-12.1
Methanol						
0.047	-0.7	0.7	-1.4	-0.5	0.1	-0.6
0.100	0.7	1.5	-0.8	1.9	0.2	1.7
0.160	4.1	2.3	1.8	4.6	0.9	3.7
0.229	5.8	3.2	2.6	6.9	1.3	5.6
0.309	5.5	3.5	2.0	5.5	1.6	3.9

mental uncertainty, but variation and the order of ΔG_t^0 values reflect a relative higher destabilisation of *cis* isomer for all the mixtures used. Complex ions have two nonpolar ethylenediamine ligands and two hydrophilic Cl^- ligands such that one can expect a participation of Coulombic as well as hydrophobic effect of ethylenediamine ligands on the solute-solvent interactions. Repulsive interactions between adjacent Cl^- ligands in *cis* isomer and the structural *trans* effect in the *trans* isomer affect the hydrophilic/hydrophobic character of the coordination sphere surface exposed to the solvent. Two Cl^- ligands are potential hydrogen bonding sites and their *cis* and *trans* positions play some role in solvation. In water, the *cis* isomer is probably better stabilised because the *cis* position of Cl^- ligands is advantageous for possible stabilisation by the intermolecular hydrogen bond between two water molecules, which hydrate Cl^- ligands. According by, we can achieve that an addition of cosolvent will lead to higher destabilisation of *cis* isomer especially in water-rich region.

The actual solvation behaviour of the complex ions is more directly represented by ΔH_t^0 and $T\Delta S_t^0$ (Table II). The transfer enthalpies of both isomers in water-organic mixtures exhibit maxima in the water-rich region (Fig. 1). The presence of ΔH_t^0 maxima in this region has been attributed to the structure-breaking effect of big complex ions and hydrophobic effect of cosolvent on the water structure. For large solutes as the complex cations, the cavity formation is the main contribution to the ΔH_t^0 . The occurrence of

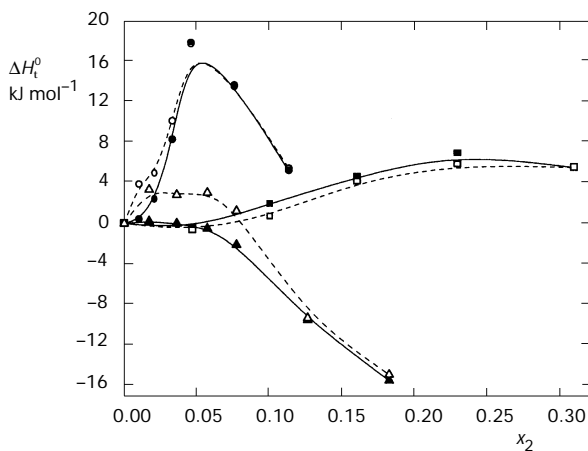


FIG. 1

Dependences of the transfer enthalpies, ΔH_t^0 , of *cis* (empty symbols) and *trans* (full symbols) isomers of $[\text{CoCl}_2(\text{en})_2]^+$ on the mole fraction of organic cosolvent, x_2 , at 298.2 K; water-*t*-BuOH (○, ●), water-MeOH (□, ■) and water-MeCN (Δ, ▲)

maxima at $x_2(t\text{-BuOH}) \approx 0.04$ and $x_2(\text{MeOH}) \approx 0.15$ has been attributed to an enhancement of water structure¹⁶. The enthalpic destabilisation is probably associated with particular difficulties in forming the solvation shell in hydrophobically ordered region of solvent. The endothermic transfer enthalpy and positive transfer entropy (Table II) point out the significant role of solvent–solvent interaction in water–alcohol mixtures. As can be seen from Fig. 1, the position and height of the maximum do not depend on the type of configuration of the complex ion. Beyond the maximum, the different charge distribution on the surface of the complex cation causes a sharper growth of the endothermic maximum of the *cis* compared with the *trans* in water–*t*-BuOH mixtures. The slopes of these curves lead to different values of McMillan–Mayer¹⁷ enthalpic pair interaction coefficients, h_{NE} , between the solute and the organic cosolvent for both isomers. In contrast to $h_{\text{NE}}(\textit{trans}) \approx -80 \text{ J kg mol}^{-2}$, a positive value $h_{\text{NE}}(\textit{cis}) \approx 1170 \text{ J kg mol}^{-2}$ was found. This suggests that the *cis* isomer interacts only weakly with the organic cosolvent but strongly with water. Figures 2 and 3 show the difference in thermodynamic behaviour of *cis*- and *trans*-[CoCl₂(en)₂]⁺.

In contrast to *t*-BuOH, in water-rich region of water–acetonitrile mixtures, the water structure remains more or less intact and the acetonitrile molecules gradually occupy the cavities between water molecules without disrupting the water structure. The limit of acetonitrile mole fraction beyond which acetonitrile can no longer be accommodated without cavities

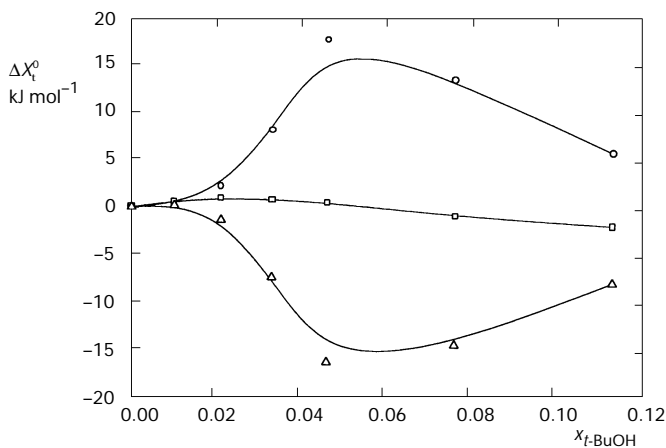


FIG. 2

Dependences of the ΔH_1^0 (○), ΔG_1^0 (□) and $-T\Delta S_1^0$ (Δ) transfer functions on *t*-BuOH mole fraction for *cis*-[CoCl₂(en)₂]⁺ at 298.2 K

in the structure of water is $x_2(\text{MeCN}) \approx 0.15$ (ref.¹⁸). Differences in ΔH_t^0 values for both ions in the water-rich region (Fig. 1) lead to different h_{NE} values: $h_{\text{NE}}(\text{cis})_{\text{MeCN}} \approx 720 \text{ J kg mol}^{-2}$ and $h_{\text{NE}}(\text{trans})_{\text{MeCN}} \approx -400 \text{ J kg mol}^{-2}$. According to these pair interaction coefficient values, a preferential solvation of $\text{trans}[\text{CoCl}_2(\text{en})_2]^+$ by cosolvent has been found. Stabilisation of the complex ions may result from ion-dipole ($\mu(\text{MeCN}) = 3.92 \text{ D}$)¹⁹ and dispersion interaction. Exothermic transfer enthalpy and negative transfer entropy especially at higher acetonitrile mole fraction (Table II) point out the predominance of solvent-solute interaction.

The partial molar volumes have been frequently used as probes of ion-solvent interaction. In water, partial molar volume for the *cis* complex is about $13 \text{ cm}^3 \text{ mol}^{-1}$ smaller than that for the *trans* one (Table I). Electrostriction for a big complex should be negligibly small, because all the charge density is very small, but charge is more localised on the surface of the *cis* isomer. Partial molar volume for *cis*- $[\text{CoCl}_2(\text{en})_2]\text{ClO}_4$ decreases monotonously with increasing mole fraction of organic cosolvent in both aqueous mixtures of acetonitrile and *tert*-butyl alcohol (Table I). For the *trans* isomer, where the preferential solvation by cosolvent was found, a maximum on the dependence of V^0 was observed at $x_2(\text{MeCN}) \approx 0.036$, $x_2(\text{t-BuOH}) \approx 0.01$.

Experimental results presented in this study show that the distribution of charge on the surface of the complex ion is an important factor in volumetric and thermodynamic behaviour of the systems studied.

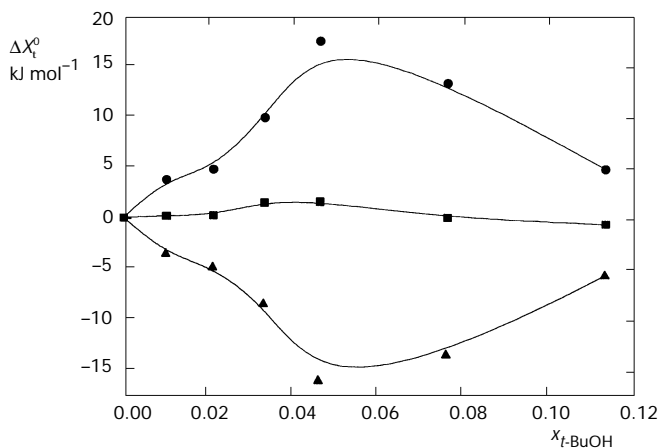


FIG. 3

Dependences of the ΔH_t^0 (●), ΔG_t^0 (■) and $-T\Delta S_t^0$ (▲) transfer functions on *t*-BuOH mole fraction for $\text{trans}[\text{CoCl}_2(\text{en})_2]^+$ at 298.2 K

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