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HEATS OF TRANSFER OF COBALT(II) PERCHLORATE FROM PURE TO MIXED SOLVENTS

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ABSTRACT

Heats of solution of solid solvates $Co(ClO_4)_2 \cdot 6L$ (L denotes the solvent molecule) in mixtures of water with *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMA), and dimethylsulphoxide (DMSO), as well as in DMA–DMSO mixtures, were measured over the entire range of solvent compositions. These data together with separately obtained differential heats of solution of solvent L in all the above mixtures enabled the determination of heats of transfer of $Co(ClO_4)_2$ from the pure to the mixed solvents. Visible absorption spectra of ternary solutions of $Co(ClO_4)_2$ in mixed solvents were also measured. The results were discussed in terms of possible ion–solvent and solvent–solvent interactions occuring in the systems investigated.

INTRODUCTION

Solvation properties of water–aprotic solvent mixtures in which strong specific interactions between components take place are markedly modified by these interactions. Cox and Natarajan [1] reported free energies, enthalpies and entropies of transfer of a variety of alkali metal and silver halides from water to DMSO–H_2O mixtures. The authors demonstrated the lack of preferential solvation in the mixtures despite significant differences in the interactions of pure DMSO and pure water with the electrolytes. Similar results were obtained for RbCl in DMF–H_2O mixtures [2]. The lack of preferential solvation in the above systems was interpreted as a result of strong hydrogen bonds between solvent components.

However, it could be expected that solvent–solvent interactions influence the solvation of divalent transition metal ions to a lesser degree because of their particularly strong interactions with the solvent molecules (covalent bonds). In this work, the preferential solvation of $Co(ClO_4)_2$ in aqueous dimethylsulphoxide, aqueous *N,N*-dimethylformamide and aqueous *N,N*-dimethylacetamide solutions was examined by determining the heats of transfer which reflect both the changes in ion–solvent and solvent–solvent interactions. For comparison, the heats of transfer of $Co(ClO_4)_2$ in *N,N*-di-

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methylacetamide–dimethylsulphoxide mixtures which do not show any specific interactions between the solvent components were also obtained.

The thermodynamic studies of transfer of divalent transition metal ions in mixed solvents are rarely reported in the literature [3–5] because of the difficulties in preparing the anhydrous salts with non-coordinating anions. The heats of transfer of $Co(ClO_4)_2$ reported in this paper were determined using the method proposed by Libuś et al. [6] for the salts occurring in the form of solvates in the solid state. In this method, the heats of solution of solid solvate were coupled with the differential heats of solution of the solvent forming the solvate.

Visible absorption spectra sensitive to the changes in the first solvation sphere of transition metal ions provided an additional support for the interpretation of the variation in the heats of transfer with solvent composition.

EXPERIMENTAL

$Co(ClO_4)_2 \cdot 6H_2O$ was obtained by dissolving cobalt(II) carbonate in perchloric acid and purified by triple crystallization from redistilled water. The crystals were dried over silica gel to stoichiometric composition, which was in the range 6.00–6.02 water molecules per cobalt(II) ion, as controlled by standard EDTA titration. $Co(ClO_4)_2 \cdot 6DMSO$ was obtained by dissolving the hydrated salt in DMSO, followed by distilling off the excess solvent under reduced pressure. The crystalline product was recrystallized twice from anhydrous DMSO and dried over P_2O_5 in a vacuum at 323 K. The number of DMSO molecules in the solvate, controlled by EDTA titration, was in the range 5.99–6.02.

DMSO, DMF, and DMA were dried over calcium hydride and purified by fractional distillation under reduced pressure. Water used in the experiments was triply distilled.

Heats of solution were determined using a calorimeter of the constant temperature–environment type, constructed in our Department by Męcik and previously described [6]. It consisted of a 1 cm^3 teflon–glass ampoule and a 100 cm^3 glass vessel contained inside a metal can, submerged in a thermostat bath kept at 298.15 ± 0.003 K. Temperature increments in the calorimeter, of the order of 10^{-2}–10^{-1} K, were measured with a 47 kΩ thermistor with a sensitivity of $\pm 5 \times 10^{-5}$ K. The heat capacity of the calorimetric system was determined electrically with an accuracy of $\pm 0.2\%$.

Heats of solution of complexes were measured at concentrations between 5×10^{-3} and 2×10^{-2} mol dm^{-3}. In this range, the concentration dependence of ΔH values was negligible compared with the experimental scatter of about 0.3 kJ mol^{-1}, so the measured heats were taken to be standard state values. The changes in composition of the mixtures during the dissolution of both the complexes and the solvents did not exceed the value of 3×10^{-3} on the mole fraction scale and were taken into account.

Concentrations of stock solutions of $Co(ClO_4)_2$ in water and DMSO were determined by standard EDTA titration. All solutions were prepared from appropriate stock solution or solvate of stoichiometric composition by weighing and their densities were measured separately by means of a bicapillary pycnometer.

Absorption spectra were measured at 298.0 ± 0.1 K using a Carl Zeiss VSU 2P spectrophotometer equipped with a thermostated cell compartment.

RESULTS

According to the method presented by Libuš et al. [6], the heat of transfer of $Co(ClO_4)_2$ between solvents L′ and L″ is determined as

$$\Delta H_{tr}[Co(ClO_4)_2]_{L' \leftarrow L''} = \Delta H^*_{s,L'} - \Delta H^*_{s,L''} \quad (1)$$

where $\Delta H^*_{s,L'}$ and $\Delta H^*_{s,L''}$ denote the heats of a hypothetical process taking place in each of these solvents

$$Co(ClO_4)_2 \cdot 6L(solid) + mL'(liq) \rightarrow (Co(ClO_4)_2 + mL')(soln) + 6L(liq) \quad (2)$$

The heat of the above process, $\Delta H^*_{s,L'}$, can be calculated from the experimental data as

$$\Delta H^*_{s,L'} = \Delta H_{s,L'} - 6\ \Delta H^L_{s,L'} \quad (3)$$

where $\Delta H_{s,L'}$ is the heat of solution of the solid solvate $Co(ClO_4)_2 \cdot 6L$ in the solvent L′ and $\Delta H^L_{s,L'}$ is the differential heat of solution of solvent L in the solution of $Co(ClO_4)_2$ in L′.

The above method can be applied provided that the solvent L from the solid complex does not affect the solvation sphere characteristic of the mixture L′, according to eqn. (2). For water–amide and water–DMSO mixtures, this condition was satisfied over the entire solvent composition range when $Co(ClO_4)_2 \cdot 6H_2O$ was used, due to the considerably weaker donor properties of water than of the organic component. Solid $Co(ClO_4)_2 \cdot$ 6DMSO was chosen for measurements in DMA–DMSO mixtures because of the high stability of its stoichiometric composition ($Co(ClO_4)_2 \cdot 6DMA$ is extremely hygroscopic). It could be used even in the DMA-rich region up to $x_{DMA} \simeq 0.97$; this was confirmed by the independence of the heats of solution on the complex concentration and also, the same heats of solution of DMSO were obtained in the presence or absence of $Co(ClO_4)_2$ in the solvent mixture.

The heats of solution of solid solvates in the binary mixtures investigated and the heats of solution of appropriate solvent (H_2O or DMSO) in

TABLE 1

Heats of solution (kJ mol^{-1}) of $Co(ClO_4)_2 \cdot 6DMSO$ and DMSO in DMA–DMSO mixtures for varying mole fractions of DMSO at 298.15 K

$Co(ClO_4)_2 \cdot 6DMSO$		DMSO	
x_{DMSO}	$\Delta H_s^\ominus$	x_{DMSO}	ΔH_s
0.030	41.02	0.006	0.68
0.043	39.03	0.063	0.63
0.058	35.92	0.115	0.58
0.099	34.46	0.182	0.47
0.178	32.22	0.275	0.36
0.272	31.65	0.397	0.27
0.394	31.72	0.558	0.13
0.555	33.80	0.745	0.06
0.599	34.11		
0.804	37.07		
1.000	40.27 [a]		

[a] Average from six measurements: 40.27 ± 0.09.

$Co(ClO_4)_2$–binary solvent systems are listed in Tables 1–3. From these data, the heats of transfer of $Co(ClO_4)_2$ from water to aqueous mixtures and from DMSO to DMA–DMSO mixtures were determined using eqns. (1) and (3).

TABLE 2

Heats of solution (kJ mol^{-1}) of $Co(ClO_4)_2 \cdot 6H_2O$ in aqueous mixtures for varying mole fractions of water at 298.15 K

$DMF–H_2O$		$DMA–H_2O$		$DMSO–H_2O$	
x_{H_2O}	$\Delta H_s^\ominus$	x_{H_2O}	$\Delta H_s^\ominus$	x_{H_2O}	$\Delta H_s^\ominus$
0.0023	−126.0	0.0026	−128.0	0.0010	−130.7
0.081	−127.8	0.051	−129.5	0.076	−131.4
0.126	−128.2	0.070	−130.2	0.197	−130.3
0.205	−127.7	0.099	−130.0	0.318	−124.1
0.293	−123.4	0.136	−128.2	0.354	−120.4
0.388	−114.3	0.177	−126.8	0.443	−111.2
0.502	−100.5	0.232	−125.1	0.540	−95.6
0.590	−84.8	0.298	−122.1	0.630	−74.9
0.700	−59.6	0.376	−117.2	0.722	−50.2
0.767	−41.5	0.432	−110.4	0.794	−28.7
0.840	−22.0	0.471	−107.4	0.854	−12.2
0.905	−6.77	0.564	−93.6	0.902	−2.37
0.916	−4.43	0.674	−72.3	0.940	3.15
0.977	5.37	0.778	−43.4	0.974	5.74
1.000	7.00 [a]	0.840	−23.7		
		0.881	−12.2		
		0.948	2.81		

[a] Average from seven measurements: 7.00 ± 0.04.

TABLE 3

Heats of solution (kJ mol^{-1}) of water in aqueous mixtures for varying mole fractions of water at 298.15 K

DMF–H_2O		DMA–H_2O		DMSO–H_2O	
x_{H_2O}	ΔH_s	x_{H_2O}	ΔH_s	x_{H_2O}	ΔH_s
0.0071	−3.33	0.0084	−5.56	0.0048	−5.15
0.085	−3.65	0.056	−5.64	0.079	−5.39
0.130	−3.80	0.075	−5.74	0.199	−5.54
0.208	−3.99	0.104	−5.78	0.319	−5.39
0.296	−4.08	0.181	−5.65	0.444	−4.86
0.391	−3.85	0.300	−5.41	0.538	−4.10
0.502	−3.37	0.379	−5.11	0.630	−3.10
0.590	−2.72	0.472	−4.61	0.723	−2.18
0.700	−1.77	0.565	−3.95	0.794	−1.20
0.767	−1.18	0.675	−2.90	0.854	−0.59
0.814	−0.80	0.779	−1.66	0.902	−0.23
0.840	−0.61	0.881	−0.55	0.940	−0.10
0.905	−0.23	0.948	−0.12	0.974	−0.086
0.916	−0.14				
0.977	−0.013				

From Tables 1 and 2, the heats of the hypothetical process (2) in pure H_2O and DMSO are equal to 7.0 and 40.3 kJ mol^{-1}, respectively. The values of $\Delta H^{L}_{s,L'}$ required for the calculation of $\Delta H^{*}_{s,L'}$ were referred to the same composition of the solvent L′ as in the case of dissolution of the complex, using interpolation curves. The heat of transfer of $Co(ClO_4)_2$ from DMSO to pure DMA was calculated as the difference between the ΔH_{tr} values from water to DMA and from water to DMSO. The results are shown in Figs. 1 and 2.

It should be noted that the heats of transfer of $Co(ClO_4)_2$ from water to pure DMF, DMA and DMSO are in good agreement with the data determined by Męcik, who used the acetonitrile-solvated salt. The respective $\Delta H^{\ominus}_{tr}$ values in kJ mol^{-1} are: −106.8 and −106.7 [6] for DMSO; −113.2 and −114.7 [7] for DMF; and −101.8 and −102.2 [7] for DMA. In contrast, the heat of transfer of $Ni(ClO_4)_2$ between water and DMA

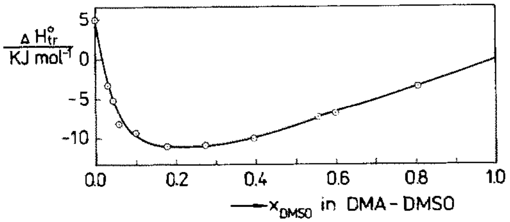

Fig. 1. Heats of transfer of $Co(ClO_4)_2$ from DMA to DMA–DMSO mixtures at 298.15 K.

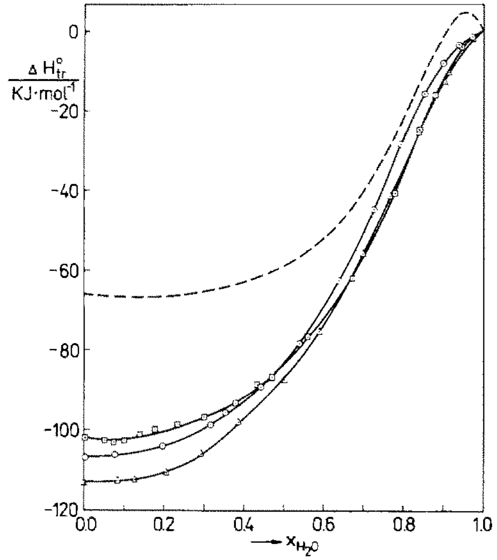

Fig. 2. Heats of transfer of $Co(ClO_4)_2$ from water to DMSO–H_2O (○), DMA–H_2O (□), DMF–H_2O (△) mixtures and heats of transfer of Co(II) ion from water to DMA–H_2O mixtures (broken line) at 298.15 K.

obtained in the same manner using $Ni(ClO_4)_2 \cdot 6AN$ [7] and that obtained directly from the heats of solution of the anhydrous salt (dehydrated by heating under vacuum) [8] differ rather markedly, the values being -94.0 and -98.8 kJ mol^{-1}, respectively.

The heats of transfer of cobalt(II) ion in DMA–H_2O mixtures can be determined from the literature data for perchlorate ion [8]. The results are presented in Fig. 2.

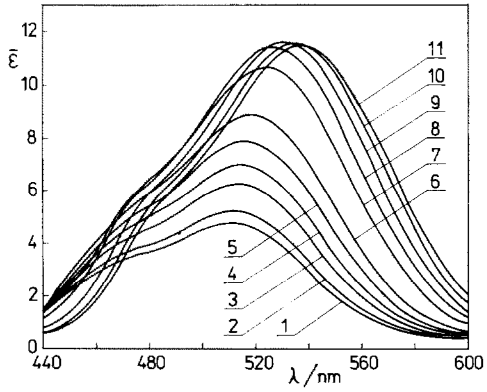

Fig. 3. Absorption spectra of ternary solutions $Co(ClO_4)_2$–DMSO–H_2O of varying solvent composition at 298.15 K. Concentration of $Co(ClO_4)_2$ is ~ 0.05 mol dm^{-3}, water mole fractions are respectively: 1, 1.0; 2, 0.965; 3, 0.894; 4, 0.855; 5, 0.805; 6, 0.759; 7, 0.648; 8, 0.555; 9, 0.385; 10, 0.196; and 11, 0.000.

Visible absorption spectra were measured for all the systems examined over the entire range of solvent composition at constant $Co(ClO_4)_2$ concentration of the order of 5×10^{-2} mol dm^{-3}. They are illustrated in Fig. 3 for the DMSO–H_2O system.

DISCUSSION

As the solvation of perchlorate ion in aprotic solvents is expected to be negligible [9], the heats of transfer of $Co(ClO_4)_2$ in DMA–DMSO mixtures may be approximately attributed to cobalt(II) ion only. The results presented in Fig. 1 show that this solvent mixture, in spite of the lack of strong specific interactions in the pure components as well as in the mixtures, cannot be regarded as close to ideal. Because of the higher donor ability of DMSO than DMA (Gutman's donor numbers are 29.8 and 27.8, respectively), the transfer of cobalt(II) ion from DMA to pure DMSO is exothermic. Therefore, the rapid decrease in $\Delta H_{tr}^{\ominus}$ on passing from DMA to DMA-rich mixtures indicates the preferential solvation of cobalt(II) ion by DMSO. However, with the increase of DMSO mole fraction (above $\simeq 0.2$), one can observe the steady increase in the heats of transfer up to the value of that in pure DMSO. The endothermic contribution to the heats of solution in this range of solvent composition seems to be associated with removing DMSO molecules from the bulk solvent structure upon solvation. Thus, the heats of transfer of Co(II) ion in DMA–DMSO mixtures reveal the bulk structure of DMSO arising from the strong but non-specific dipole–dipole interactions found in this solvent [10].

The above interpretation of the calorimetric results agrees with the spectrophotometric data for the $Co(ClO_4)_2$–DMA–DMSO system. On passing from DMA to DMSO solution, the visible absorption band of cobalt(II) solvation complexes changes only in its intensity, the changes being most pronounced in the DMA-rich region and almost negligible in the DMSO-rich region. It suggests the preferential solvation of cobalt(II) ion by DMSO over the entire range of solvent composition.

In contrast to the DMA–DMSO mixtures, the aqueous binary mixtures investigated in this work show strong solvent structure arising from intercomponent hydrogen bonds, with maximum interactions at a water mole fraction of about 0.6–0.7 [11–14]. As can be seen from Fig. 2, there is a similarity between the variation in heats of transfer for $Co(ClO_4)_2$ in the three mixtures investigated. This may result from similar donor properties of the organic components as well as from their similar interactions with water. Also the contribution of the perchlorate ion to the heats of transfer is expected to be similar in these mixtures.

The strongly exothermic transfer of Co(II) ion from water to pure organic solvent results both from the stronger donor properties of the organic component compared with those of water (Gutman's donor numbers of water and DMF are 18.1 and 26.6, respectively) and from the much stronger bulk structure of water compared with aprotic solvents. The endothermic transfer of Co(II) ion from water to water-rich mixtures may thus reflect the increase in the structure of mixed solvent, as was indicated for sodium ion in the DMSO–H_2O system [15]. The rapid decrease in $\Delta H_{tr}^{\ominus}$ with the further increase of organic solvent content (up to $x_{H_2O} \simeq 0.6$), in spite of the expected increase of the endothermic "structural" contribution to the heats of transfer, indicates the strong replacement of water molecules by organic solvent in the first solvation sphere of cobalt(II) ion.

This explanation is supported by the relatively marked changes in the absorption spectra with increase of the organic solvent content, which reflects the marked changes in the Co(II) ion coordination sphere. The effect for the DMSO–H_2O system is shown in Fig. 3.

In contrast, the trend in $\Delta H_{tr}^{\ominus}$ values in organic solvent-rich mixtures (up to $x_{H_2O} \simeq 0.4$) might suggest that the coordination sphere of Co(II) ion remains almost unchanged. However, in this solvent composition range, the endothermic contribution to the heats of transfer is expected to increase on passing from practically unstructured aprotic solvent (intermolecular interactions in DMSO are markedly weaker than hydrogen bonds) to its well structured mixtures with water. This would imply the increased solvation of Co(II) ion in the mixtures compared with that in pure organic solvent.

On the other hand, the absorption spectra show that water molecules do enter the coordination sphere of the cobalt(II) ion, even in the organic solvent-rich region; the effect is weakest in DMSO–H_2O mixtures (because of the strong donor ability of DMSO) and the strongest in DMA–H_2O mixtures (probably because of a reduction in the donor ability of DMA in the octahedral $Co(DMA)_6^{2+}$ complex due to hindrance).

The calorimetric and spectrophotometric results may be compatible if we assume that the increased solvation interactions arise from hydrogen bonds between coordinated water and organic solvent molecules from the second solvation sphere of the cobalt(II) ion.

The results presented suggest that Co(II) ion is preferentially solvated by the organic component in the aqueous mixtures under study, except perhaps in the water-rich region.

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