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Enthalpies of transfer of cobalt(II) perchlorate from water to alcohol–water mixtures

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Abstract

The enthalpies of solution of solid $Co(ClO_4)_2 \cdot 6H_2O$ and of water have been measured in binary mixtures of water with some alcohols (methanol, ethanol, 1-propanol and ethylene glycol) over the whole range of solvent composition. These data have been used for calculations of the enthalpies of transfer of $Co(ClO_4)_2$ from water to the mixtures. In the ethanol-rich mixtures, an alternative method of determining the enthalpies of transfer has also been applied. Electronic absorption spectra of ternary solutions of $Co(ClO_4)_2$ in mixed solvents have been measured as an aid in the interpretation of the calorimetric data.

INTRODUCTION

Enthalpies of transfer of salts from pure to mixed solvents give valuable information about the solvation properties and structures of the mixtures. Salts of divalent transition metal ions seem to be especially suitable subjects for these investigations because of strong ion–solvent interactions. Moreover these salts exhibit visible absorption spectra that are sensitive to the changes in the solvation sphere, and thus provide additional support for the interpretation of the enthalpies of transfer in mixed solvents.

Despite the above advantages, there is a lack of data for enthalpies of transfer of transition metal salts in alcohol–water mixtures, probably because of difficulties in obtaining anhydrous salts with non-coordinating anions. The enthalpies of transfer of $Co(ClO_4)_2$ from water to alcohol–water mixtures reported in this paper were determined using the method described earlier [1, 2] from the enthalpies of solution of solid hydrate $Co(ClO_4)_2 \cdot 6H_2O$ and the enthalpies of solution of water

$$\Delta H_t^{\ominus}[Co(ClO_4)_2]_{H_2O \to xH_2O} = \Delta H_s^{\ominus}[Co(ClO_4)_2 \cdot 6H_2O]_{xH_2O} - 6\Delta H_s^{\ominus}(H_2O)_{xH_2O} - \Delta H_s^{\ominus}[Co(ClO_4)_2 \cdot 6H_2O]_{H_2O} \quad (1)$$

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where x_{H_2O} denotes the mole fraction of water in the mixture to which the salt is transferred.

For the ethanol-rich mixtures, an alternative method was applied. It consists of measuring the heats of mixing of equal amounts of water with both aqueous (or pure) alcohol q, and with $Co(ClO_4)_2$ solution of the same solvent composition q_s. The difference in the heats of the two above processes, referred to one mole of $Co(ClO_4)_2$, gives the enthalpy of transfer of the salt between solvents of initial x_i and final x_f water mole fraction

$$\Delta H_t[Co(ClO_4)_2]_{x_i \to x_f} = (q_s - q)/n \qquad (2)$$

where n denotes the amount of substance of $Co(ClO_4)_2$ in the solution.

EXPERIMENTAL

All alcohols used in the study were analytical grade, produced by POCh, Poland. Methanol was purified by heating with magnesium and iodine, followed by distillation. Ethanol and 1-propanol were kept over 3 Å molecular sieves and then distilled. Ethylene glycol, dried with 3 Å molecular sieves, was purified by fractional distillation under reduced pressure. All distillations were carried out using a Vigreux column. Water was twice distilled just before use.

Solid $Co(ClO_4)_2 \cdot 6H_2O$ was obtained and kept as described previously [1,2].

Anhydrous solutions of $Co(ClO_4)_2$ in ethanol were obtained as described by Diamond et al. [3] by dissolving the hydrated salt in dry alcohol, keeping the solutions over 3 Å molecular sieves for a day, followed by boiling for 30 min. After cooling, solutions were filtered and their concentrations were determined by standard EDTA titration.

The enthalpies of solution were measured using a precise calorimeter of the constant-temperature-environment type, described previously [4]. Temperature increments in the calorimeter were measured with a quartz sensor, which is particularly suitable in reaction calorimetry because of its linear response and long-time stability. The frequencies of the electronic oscillator, determined by the quartz sensor, were measured using a digital frequency meter connected via an interface with an Amstrad CPC 6128 microcomputer, in which frequency data were stored. The sensitivity of the temperature measurements was $\pm 5 \times 10^{-5}$ K.

Total temperature changes were calculated using a computer program based on Newton's cooling rule. The program, written in BASIC, uses a linear approximation of the temperature run during the initial period and an exponential function during the final period. To check the accuracy of the temperature measurement system, two series of 7–8 electrical calibrations each, for total temperature changes of 0.15 K and 0.03 K, were made. The reproducibility of the electrical calibration was 0.07% and 0.14%, respectively.

The enthalpies of solution of $Co(ClO_4)_2 \cdot 6H_2O$ were found to be independent of salt concentration in the range 10^{-3}–10^{-2} mol dm^{-3}; therefore they were taken as the standard values. The reproducibility of the $\Delta H_s^\ominus$ values was 0.3 kJ mol^{-1}. The changes in composition of the mixtures connected with the dissolution of both the hydrate and water did not exceed the value of 3×10^{-3} on the mole fraction scale.

Electronic absorption spectra of $Co(ClO_4)_2$–alcohol–water solutions for various solvent compositions were measured using a Beckman UV 5270 spectrophotometer at 298.15 ± 0.1 K.

RESULTS AND DISCUSSION

The enthalpies of solution of solid $Co(ClO_4)_2 \cdot 6H_2O$ in alcohol–water mixtures are listed in Table 1 and the enthalpies of solution of water in the mixtures are listed in Table 2 and shown in Fig. 1. The enthalpies of transfer of $Co(ClO_4)_2$ were calculated from the above data using eqn (1). The enthalpies of solution of water required for the calculation of $\Delta H_t^\ominus$ were referred to the same composition of the mixture as in the case of dissolution of the hydrate, by means of interpolation curves. The results are presented in Fig. 2.

The heats of mixing of water with ethanol–water mixtures q, and with $Co(ClO_4)_2$–ethanol–water solutions q_s, are listed in Table 3. The enthalpies of transfer of $Co(ClO_4)_2$ from ethanol to the ethanol-rich mixtures, calculated using eqn. (2), are presented in Table 3 and Fig. 2. As can be seen from Fig. 2, the dependence of $\Delta H_t^\ominus$ on x_{H_2O} for the ethanol–water system obtained by both methods shows a minimum at the same mole fraction of water (approx. 0.05), whereas the depth of the minimum differs by about 2 kJ mol^{-1}.

The enthalpies of transfer of $Co(ClO_4)_2$ from water to the aqueous alcohols may be considered as a sum of two main contributions. The first contribution results from replacement of water molecules by alcohol molecules in the solvation sphere of the ions, and the second results from the disruption of solvent ordering by ions to form the solvation sphere.

The endothermic maxima on the $\Delta H_t^\ominus$ versus x_{H_2O} dependence in the water-rich region, also observed for alkali and alkaline earth metal salts [5–8], are regarded as resulting from the enhancement of the three-dimensional structure of water by small amounts of alcohol. As can be seen from Fig. 2, this effect is stronger for 1-propanol and ethanol than for methanol because of the stronger hydrophobic character of the propyl and ethyl groups compared to the methyl group; the effect is minimal for

TABLE 1

Enthalpies of solution of $Co(ClO_4)_2 \cdot 6H_2O$ in alcohol–water mixtures for various mole fractions of water at 298.15 K

x_{H_2O}	$\Delta H_s^\ominus$/kJ mol^{-1}	x_{H_2O}	$\Delta H_s^\ominus$/kJ mol^{-1}
1.0	7.00	1-Propanol–water	
Methanol–water		0.980	12.31
0.953	9.78	0.954	16.31
0.890	12.31	0.932	15.19
0.826	8.98	0.926	14.13
0.704	−2.26	0.857	7.29
0.608	−10.09	0.775	−0.54
0.494	−19.36	0.605	−14.75
0.408	−25.51	0.403	−23.61
0.302	−34.16	0.223	−24.49
0.199	−43.92	0.145	−23.14
0.106	−54.70	0.103	−22.79
0.002	−65.87	0.055	−21.12
Ethanol–water		0.019	−17.91
0.980	19.15	0.003	−10.22
0.941	13.70	Ethylene glycol–water	
0.902	16.00	0.955	6.83
0.871	14.54	0.903	5.71
0.853	11.43	0.805	−1.84
0.795	2.00	0.709	−10.83
0.673	−10.40	0.600	−19.42
0.599	−15.96	0.497	−26.92
0.491	−22.06	0.375	−34.05
0.381	−26.87	0.207	−40.92
0.300	−29.37	0.105	−43.46
0.205	−32.61	0.054	−43.96
0.200	−32.36	0.029	−45.50
0.163	−33.81	0.002	−43.30
0.102	−36.59		
0.057	−39.70		
0.016	−41.18		
0.002	−39.21		

ethylene glycol whose molecule shows rather weak hydrophobic properties [9].

The exothermicity of the transfer of $Co(ClO_4)_2$ from water to the aqueous alcohols, apart from the water-rich region, mainly reflects the reduction of solvent–solvent interactions in the mixtures compared with those in pure water. However, the sequence of $\Delta H_t^\ominus$ values from water to

TABLE 2

Enthalpies of solution of water in alcohol–water mixtures for various mole fractions of water at 298.15 K

x_{H_2O}	$\Delta H_s^\ominus$/kJ mol^{-1}	x_{H_2O}	$\Delta H_s^\ominus$/kJ mol^{-1}
Methanol–water		1-Propanol–water	
0.953	−0.035	0.980	−0.024
0.891	−0.20	0.954	−0.08
0.814	−0.49	0.932	−0.37
0.698	−0.86	0.926	−0.40
0.611	−1.05	0.858	−0.48
0.498	−1.16	0.776	−0.46
0.304	−1.45	0.609	−0.38
0.201	−1.77	0.408	0
0.108	−2.27	0.227	0.72
0.004	−3.00	0.151	0.89
Ethanol–water		0.105	0.82
0.980	−0.01	0.059	0.71
0.941	−0.05	0.023	0.38
0.902	−0.33	0.007	−0.56
0.854	−0.70	Ethylene glycol–water	
0.798	−0.92	0.956	−0.039
0.675	−1.00	0.905	−0.16
0.602	−0.97	0.806	−0.44
0.387	−0.71	0.711	−0.68
0.285	−0.58	0.603	−0.88
0.210	−0.59	0.379	−1.25
0.167	−0.65	0.211	−1.52
0.104	−0.98	0.090	−1.74
0.061	−1.31	0.058	−1.80
0.019	−1.74	0.032	−1.86
0.003	−2.01	0.006	−1.90

pure alcohols and the variation of $\Delta H_t^\ominus$ in the alcohol-rich region, in which the bulk structure of solvent is not expected to change markedly, can be explained by differences in ion–solvent interactions. The decrease in $\Delta H_t^\ominus$ with increasing water content reflects the exothermic replacement of alcohol molecules in the solvation sphere of the Co(II) ion by water molecules, indicating preferential hydration of Co(II) ion in aqueous alcohols. This effect diminishes in the order: 1-propanol > ethanol > ethylene glycol. It is not noticeable in the case of methanol whose solvating properties are fairly similar to those of water [10].

The shape and position of the absorption bands of the electronic spectra of $Co(ClO_4)_2$ solutions are almost independent of solvent composition, as

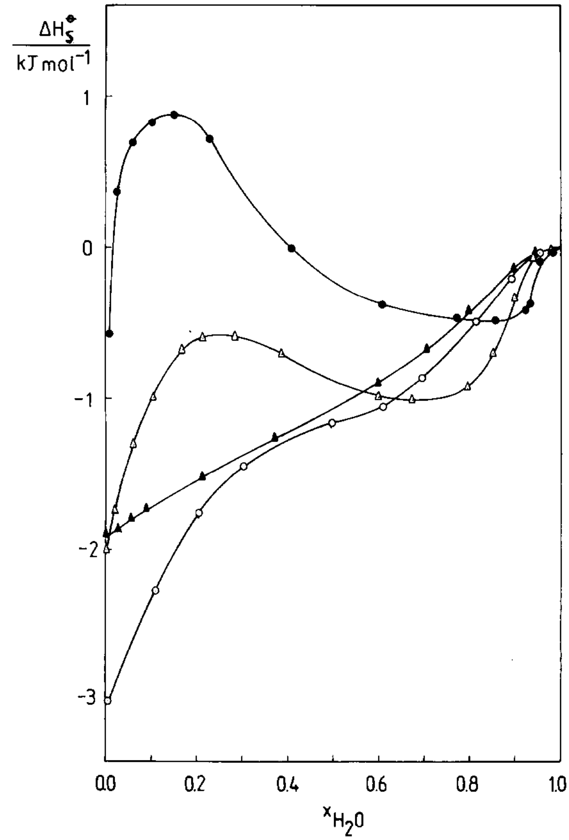

Fig. 1. Enthalpies of solution of water in alcohol–water mixtures at 298.15 K: ○, methanol–water; △, ethanol–water; ●, 1-propanol–water; ▲, ethylene glycol–water.

can be seen from Fig. 3 for the propanol–water system. Thus, the variation in the mean molar absorption coefficient ($\bar{\varepsilon}_{\lambda_{max}}$) with solvent composition (Fig. 3) mainly reflects the changes in the symmetry of the approximately octahedral arrangement of ligands around the Co(II) ion. This effect is smallest for methanol because of the similarity between methanol and water molecules, and it is greatest for ethylene glycol for steric reasons. However, the strong decrease in $\bar{\varepsilon}_{\lambda_{max}}$ values on addition of small amounts of water to propanol and ethanol suggests that alcohol molecules from the solvation sphere of the Co(II) ion are exchanged for water molecules much more easily than in the case of methanol and ethylene glycol, for which changes in the intensity of the absorption band are small in the alcohol-rich region. This conclusion is consistent with the calorimetric results.

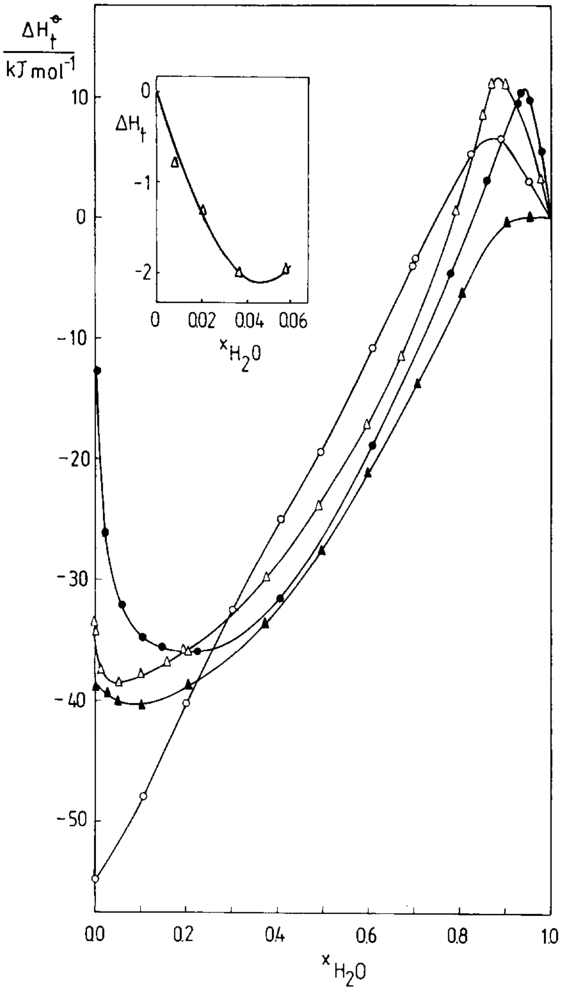

Fig. 2. Enthalpies of transfer of $Co(ClO_4)_2$ from water to alcohol–water mixtures at 298.15 K: ○, methanol–water; △, ethanol–water; ●, 1-propanol–water; ▲, ethylene glycol–water. Inset: enthalpies of transfer of $Co(ClO_4)_2$ from ethanol to ethanol–water mixtures (see Table 3).

TABLE 3

Heats of mixing of water with ethanol–water mixtures q and with $Co(ClO_4)_2$–ethanol–water solutions q_s, and the enthalpies of transfer of $Co(ClO_4)_2$ from ethanol to ethanol–water mixtures at 298.15 K

x_i [a]	x_f [a]	q_s/J	q/J	$\Delta H_{t,x_i \to x_f}$/kJ mol^{-1}	$\Delta H_{t,EtOH \to x_f}$/kJ mol^{-1}
0	0.0081	30.31	32.69	−0.76	−0.76
0.0081	0.0217	47.15	48.80	−0.53	−1.29
0.0217	0.0385	54.23	56.16	−0.71	−2.00
0.0385	0.0566	60.63	60.43	0.07	−1.93

[a] Mole fraction of water. The concentration of $Co(ClO_4)_2$ was approx. 0.02 mol dm^{-3}.

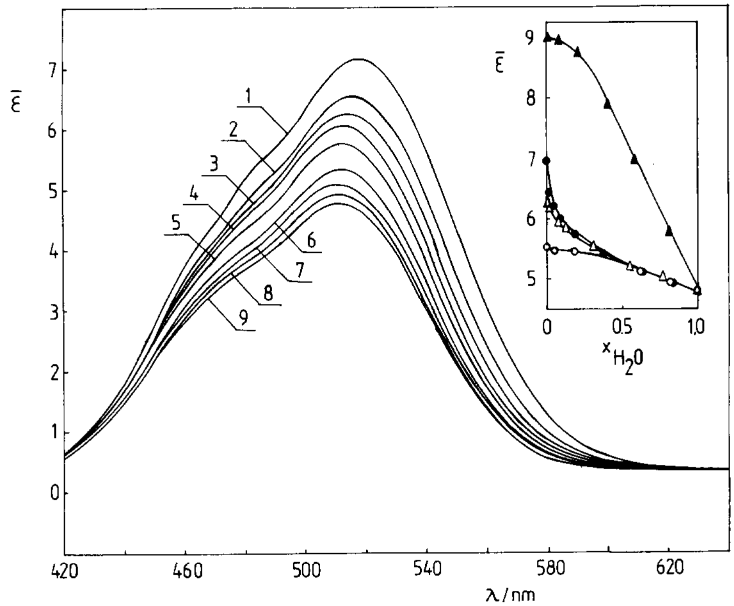

Fig. 3. Absorption spectra of ternary solutions $Co(ClO_4)_2$–1-propanol–water of varying solvent composition at 298.15 K. The concentration of $Co(ClO_4)_2$ was approx. 0.03 mol dm^{-3}, with water mole fractions: 1, 0.000; 2, 0.015; 3, 0.039; 4, 0.092; 5, 0.195; 6, 0.365; 7, 0.641; 8, 0.809; 9, 1.0. The inset shows the mean molar absorption coefficients versus water mole fraction in the mixtures: ○, methanol–water; △, ethanol–water; ●, 1-propanol–water; ▲, ethylene glycol–water.

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REFERENCES

1 E. Kamieńska-Piotrowicz, Thermochim. Acta, 143 (1989) 161.
2 E. Kamieńska-Piotrowicz, Bull. Pol. Acad. Sci Chem., 37 (1989) 87.
3 A. Diamond, A. Fanelli and S. Petrucci, Inorg. Chem., 12 (1973) 611.
4 E. Kamieńska-Piotrowicz and H. Inerowicz, J. Chem. Soc. Faraday Trans., 86 (1990) 3391.
5 E. Valera, D. Feakins and W.E. Waghorne, J. Chem. Soc. Faraday Trans. 1, 76 (1980) 560.
6 S. Taniewska-Osińska and J. Barczyńska, J. Chem. Soc. Faraday Trans. 1, 80 (1984) 1409.
7 M.H. Abraham, T. Hill, H.C. Ling, R.A. Schulz and R.A.C. Watt, J. Chem. Soc. Faraday Trans. 1, 80 (1984) 489.
8 S. Taniewska-Osińska, J. Barczyńska and B. Pałecz, Thermochim. Acta, 160 (1990) 303.
9 J.Y. Huot, E. Battistel, R. Lumry, G. Villeneuve, J. Lavallee, A. Anusiem and C. Jolicoeur, J. Solution Chem., 17 (1988) 601.
10 M. Johnsson and I. Persson, Inorg. Chim. Acta, 127 (1987) 15.