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THERMOCHEMISTRY OF COPPER(II) ION SOLVATION IN AQUEOUS ORGANIC SOLVENTS

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Abstract

The integral heat effects of $CuCl_2$ dissolution in aqueous DMSO, aqueous ethanol and aqueous acetone solutions at 298.15 K in the electrolyte concentration range 0.001–0.01 *M* were measured by means of calorimetry. ΔH^0_{sol} values were obtained by extrapolation to zero electrolyte concentration. Literature data were used to determine the thermodynamic characteristics of Cu^{2+} transfer from water to aqueous organic solvents.

Keywords: copper(II) chloride, heat effects of dissolution, ion solvation, thermochemistry, water–organic solvents

Introduction

Thermodynamic data on *d*-metal ion solvation in different media are of great value for determination of the regularities of the nature of the influence of the solvent on the heat effects of complex formation reactions.

The present paper reports the results of thermochemical determination of $\Delta_t H^0$ for copper(II) ion in aqueous acetone, aqueous ethanol and aqueous dimethylsulphoxide mixtures.

Experimental

The heat effects of $CuCl_2$ dissolution ($\Delta_s H^m$) in mixtures of water and different organic solvents were measured with a microcalorimeter with an isothermal shell [1] at 298.15 K in the electrolyte concentration range 0.001–0.01 *M*. The heat effects of $CuCl_2$ dissolution were extrapolated to zero electrolyte concentration to give $\Delta_s H^0$ values. The transfer enthalpy changes of copper(II) ion were determined by using well-known $\Delta_t H^0$ for the chloride ion [2, 3].

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Results and discussion

Primary experimental data are presented in Table 1. Standard values of solution enthalpies ($\Delta_s H^0$) were obtained by extrapolation of $\Delta_s H^m$ to zero electrolyte concentration. In can be seen from Table 1 that the value of $\Delta_s H^m$ changes differently as the $CuCl_2$ concentration is varied. This shows that the contributions of interionic interactions and structural reconstruction of the solution to $\Delta_s H^m$ differ for each solvent.

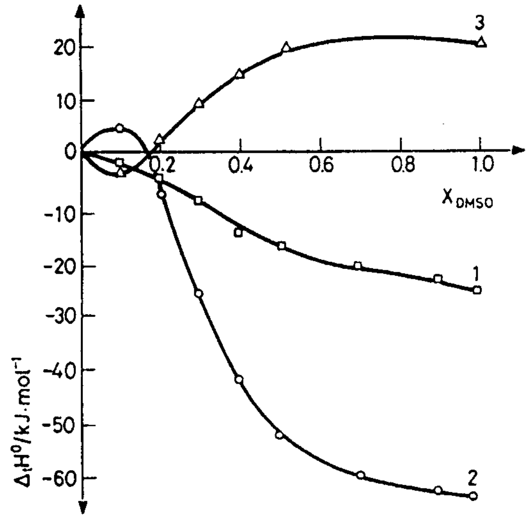

Fig. 1 Transfer enthalpies of stoichiometric mixtures (Cu^{2+} + $2Cl^-$) (1) and individual ions of Cu^{2+} (2) and Cl^- (3) from water to water – DMSO mixtures

The transfer enthalpies of copper(II) ion, chloride ion and $\Sigma(Cu^{2+} + 2Cl^-)$ in aqueous DMSO solvents are given in Fig. 1. In can be seen that the increase in the exothermicity of $CuCl_2$ dissolution with increase of the DMSO concentration is determined by a large increase in the exothermicity of copper(II) ion solution; it is not compensated by an endothermic contribution of $\Delta_t H^0_{Cl^-}$.

The results obtained and the literature data on $\Delta_s G^0_{Cu^{2+}}$ [4, 5] for copper(II) ion solvation permitted estimation of the main thermodynamic characteristics of copper(II) ion transfer from water into its mixtures with DMSO, ethanol and acetone (Fig. 2). Aqueous organic solvents influence $\Delta_t G^0_{Cu^{2+}}$ in different ways.

The stabilization of copper(II) ion is observed only in mixtures of water and a highly coordinating solvent, DMSO. Acetone and ethanol additions to water result in copper(II) ion destabilization in solution. However, in aqueous acetone solutions the enthalpy changes increase the interactions between the ions and the molecules of solvent, while in aqueous ethanol solutions both energetic and

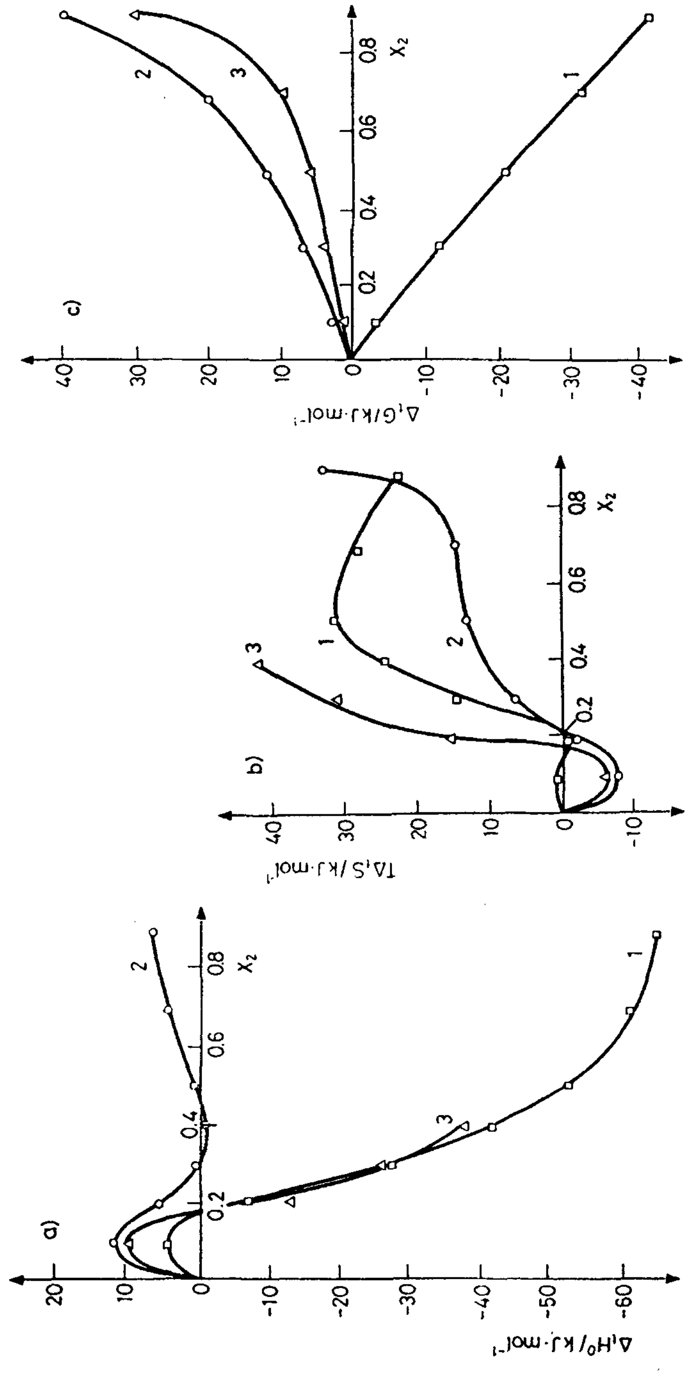

Fig. 2 Transfer thermodynamics of copper(II) ion from water to water–DMSO (1), water–ethanol (2) and water–acetone (3) mixtures

Table 1 Experimental data of calorimetric studies on heat effects of $CuCl_2$ dissolution in the mixtures of water and different organic solvents at 298.15 K

Mole fr. org. solvent (x_2)	$m\times10^3$ / mol·kg^{-1}	$\Delta_sH^m\pm0.1$	$\Delta_sH^\circ\pm0.3$
		kJ·mol^{-1}	
	DMSO		
0.0	1.758	51.40	50.9
	2.584	51.42	
	4.107	51.48	
	7.894	51.88	
0.1	0.918	53.88	53.4
	2.973	54.25	
	3.434	54.33	
	6.107	54.62	
0.2	1.019	55.62	55.2
	2.703	55.58	
	5.979	55.87	
	7.001	56.12	
0.3	1.049	58.89	59.3
	1.648	58.78	
	2.854	58.43	
	7.354	58.10	
0.4	1.057	64.42	65.3
	1.665	64.25	
	2.181	64.08	
	2.822	63.88	
0.5	0.912	66.18	67.0
	1.645	65.72	
	2.448	65.73	
	2.976	65.42	
0.7	0.907	71.16	72.2
	1.344	71.00	
	2.551	70.70	
	3.483	70.11	
0.9	0.962	74.23	74.6
	1.502	73.92	
	2.784	73.82	
	4.454	73.60	

Table 1 Continued

Mole fr. org. solvent (x_2)	$m\times10^3$ / $mol\cdot kg^{-1}$	$\Delta_s H^m\pm0.1$	$\Delta_s H^\circ\pm0.3$
		kJ·mol^{-1}	
	ethanol		
0.1	1.025	47.24	46.7
	2.223	48.03	
	3.466	48.19	
	6.654	48.50	
0.2	0.752	45.87	45.4
	2.268	46.08	
	4.762	46.28	
	6.450	46.54	
0.3	0.707	45.02	44.4
	2.648	45.21	
	3.783	45.46	
	6.571	45.83	
0.4	1.190	43.84	43.3
	2.481	44.00	
	3.772	44.25	
	6.699	44.57	
0.5	1.126	43.11	42.6
	2.524	43.58	
	4.527	43.51	
	6.786	43.74	
0.7	0.986	40.78	40.4
	2.501	41.06	
	4.256	41.26	
	8.294	41.51	
0.9	0.812	38.85	38.5
	2.209	39.12	
	3.900	39.38	
	8.012	39.69	
	acetone		
0.1	1.002	50.12	51.1
	2.177	49.54	
	4.789	48.97	
	7.656	48.31	

Table 1 Continued

Mole fr. org. solvent (x_2)	$m\times10^3$ / mol·kg^{-1}	$\Delta_s H^m \pm 0.1$	$\Delta_s H^\circ \pm 0.3$
		kJ·mol^{-1}	
	acetone		
0.2	1.023	49.80	50.7
	2.621	49.26	
	3.890	48.83	
	2.051	49.29	
	6.479	48.59	
0.3	1.288	49.55	50.5
	5.755	48.64	
	8.026	48.20	
0.4	0.825	49.10	49.7
	2.113	48.74	
	4.864	48.25	
	7.944	47.72	

structural changes in the solution lead to destabilization of the ion. This can be explained by the structural features of the aqueous ethanol solvent.

During nickel(II) ion solvation in aqueous ethanol solvent, the value of $\Delta_t H^0_{Ni^{2+}}$ is negative and metal ion destabilization in solution is not observed [6]. It can be considered that copper(II) ion solvatocomplex formation in aqueous ethanol solutions is accompanied by more intense changes of interparticle interactions in the solution than those for nickel(II) ion solvatocomplex formation.

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Zusammenfassung — Mittels Kalorimetrie wurden die integralen Wärmeeffekte des Lösens von $CuCl_2$ in wäßrigen DMSO-, wäßrigen Ethanol- und wäßrigen Acetonlösungen bei 298.15 K im Elektrolytkonzentrationsbereich 0.001–0.01 *M* gemessen. Die ΔH^0_{sol} Werte wurden durch Extrapolation auf die Elektrolytkonzentration 0 erhalten. Unter Verwendung von Angaben aus der Literatur wurde eine thermodynamische Charakterisierung des Übergangs der Cu^{2+}-Ionen vom Wasser in die wäßrigen organischen Lösungsmittel bestimmt.