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# THERMOCHEMISTRY OF FORMATION OF COPPER(II)-ETHYLENEDIAMINE COMPLEXES AND SOLVATION OF REAGENTS IN AQUEOUS ORGANIC SOLVENTS

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## Abstract

The heat effects of the reactions of formation of ethylenediamine-copper(II) complexes were determined calorimetrically in mixtures of water with ethanol, acetone and dimethylsulfoxide. The results were interpreted in terms of the enthalpies of transfer ($\Delta_t H^0$) of the complex former, the ligand and the complex ion from water to binary solvents.

In water – DMSO mixtures, the $\Delta_t H^0$ values for copper(II) and complex ions were found to change in similar ways, and their contributions to the reaction heat effects compensate each other to a large extent. Thus, the reaction enthalpy change due to solvent composition variation is caused mainly by the changes in ligand solvation enthalpies.

In aqueous ethanol and acetone solutions, the changes in $\Delta_t H^0$ for all reagents influence the heat effect equally.

**Keywords**: binary solvents, copper(II) complexes with ethylenediamine, reaction heat effects, thermochemistry, transfer heat of reagents

## Introduction

The choice of the medium in which to carry out various chemical processes is difficult at present due to the lack of knowledge of the general regularities of the influence of the solvent on the thermodynamic characteristics and kinetics of the reactions.

Attempts to solve this problem by establishing the relationships between the stability constants or heat effects of the reactions and various properties of the medium lead to dependences of a particular character only. This is due to the fact that the shift in the chemical equilibrium and the variation in the heat effect of the reaction with the nature and composition of the solvent depend on the different extents of its influence on the Gibbs energy and solvation enthalpy of each particle taking part in the reaction. Establishment of the interrelationship between the reagent solvation and the thermodynamic characteristics of the processes is therefore a fundamental problem in both theoretical and applied

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chemistry. The solution of this problem requires a number of experimental data on solvation and complex formation in different media.

In our laboratory, many experimental data on the heat effects of reactions and reagent solvation have been obtained for the complex formation reactions of nickel(II) ions with amines [1–3]. For these reactions, it was demonstrated that, in the absence of the specific interactions in the solution, the limit of the enthalpy changes of the reactions did not exceed the transfer enthalpy change of the ligand, and the influence of aqueous organic solvents on the heat effects of the reactions was basically due to the enthalpy change of amine solvation.

However, these regularities can not be assigned *a priori* to the complexes of other transition metals without some additional study.

This paper presents the results of thermochemical analysis of the reactions of formation of ethylenediamine-copper(II) monocomplexes in certain aqueous organic solvents, based on the experimental determination of the heat effects of the reactions and the enthalpies of reagent transfer ($\Delta_t H^0$) from water to differ-

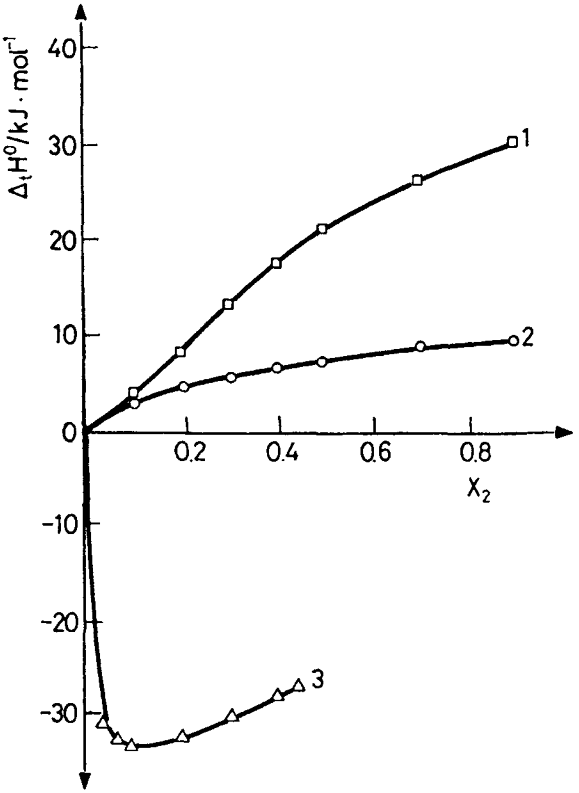

**Fig. 1** Variation in $\Delta_t H^0$ of ethylenediamine in aqueous solutions of dimethylsulfoxide (1), ethanol (2) and acetone (3)

ent binary solvents (water–ethanol, water–acetone and water–dimethylsulfoxide mixtures).

## Experimental

The $\Delta_t H^0$ values of copper(II) ions were presented and discussed in a previous paper [4]. The enthalpies of transfer of ethylenediamine from water to the binary solvents ($\Delta_t H^0_{\mathrm{En}}$) were calculated on the basis of the heat effects of amine dissolution in the whole composition range of the aqueous organic solvents, the acid-base equilibria in the solution being taken into account. All these problems were considered in detail earlier [1, 2, 5]. In the present paper, it should be noted that in aqueous dimethylsulfoxide and ethanol solutions (Fig. 1) there is a gradual decrease in the exothermicity of ethylenediamine solvation ($\Delta_t H^0_{\mathrm{En}}>0$). The characteristic features of ligand solvation in aqueous acetone solutions are related to the chemical interaction between the solute (En) and the non-aqueous component of the solvent [6, 7].

Heats of complex formation were determined by using a calorimeter of our own design and a device with a titration block, similar to that described previously [8]. The calorimetric vessel contained aqueous organic solutions of copper(II) perchlorate ($5\times10^{-2}$ mol·dm$^{-3}$). Anhydrous ethylenediamine was injected in small amounts into these solutions by using a syringe tube with a micro-screw. In this case the total enthalpy of mixing ($\Delta_{\mathrm{mix}}H$) contains the contributions of the heat effects of the following reactions:

$$\mathrm{Cu}^{2+}_{(\mathrm{soln})}+\mathrm{En}_{(\mathrm{soln})} \xrightarrow{\Delta_r H_1} [\mathrm{CuEn}]^{2+}_{(\mathrm{soln})} \qquad (1)$$

$$\mathrm{Cu}^{2+}_{(\mathrm{soln})}+2\mathrm{En}_{(\mathrm{soln})} \xrightarrow{\Delta_r H_2} [\mathrm{CuEn}_2]^{2+}_{(\mathrm{soln})} \qquad (2)$$

$$\mathrm{Cu}^{2+}_{(\mathrm{soln})}+3\mathrm{En}_{(\mathrm{soln})} \xrightarrow{\Delta_r H_3} [\mathrm{CuEn}_3]^{2+}_{(\mathrm{soln})} \qquad (3)$$

$$\mathrm{En}_{(\mathrm{soln})} + \mathrm{H}^{+}_{(\mathrm{soln})} \xrightarrow{\Delta_{\mathrm{pro}} H_1} \mathrm{EnH}^{+}_{(\mathrm{soln})} \qquad (4)$$

$$\mathrm{EnH}^{+}_{(\mathrm{soln})} + \mathrm{H}^{+}_{(\mathrm{soln})} \xrightarrow{\Delta_{\mathrm{pro}} H_2} \mathrm{EnH}^{2+}_{2(\mathrm{soln})}\ (\mathrm{soln}) \qquad (5)$$

$$\mathrm{H_2O} \xrightarrow{\Delta_{\mathrm{ion}} H} \mathrm{H}^{+} + \mathrm{OH}^{-} \qquad (6)$$

$$\mathrm{En}_{(\mathrm{liq})} \xrightarrow{\Delta_{\mathrm{sol}} H} \mathrm{En}_{(\mathrm{soln})} \qquad (7)$$

The heats of the ethylenediamine protonation reactions ($\Delta_{\mathrm{pro}} H_{1,2}$) and of the solvent ionization ($\Delta_{\mathrm{ion}} H$) have been found to be the same, but opposite in sign

[9, 10]. The maximum difference in the heat effects for these processes was 0.5 kJ·mol$^{-1}$, and the fraction of the EnH$^{+}$ and EnH$_2^{2+}$ forms was not more than 0.1% of the total quantity of ethylenediamine in solution. The contributions of $\Delta_{pro}H_{1,2}$ and $\Delta_{ion}H$ were therefore not taken into account.

The $\Delta_r H_{1,2,3}$ values were calculated by using the system of equations of the following type:

$$\Sigma\Delta_r H^{(i)} = \Delta\alpha_1^{(i)}\Delta_r H_1 + \Delta\alpha_2^{(i)}\Delta_r H_2 + \Delta\alpha_3^{(i)}\Delta_r H_3 \qquad (7)$$

where

$$\Sigma\Delta_r H^{(i)} = \Delta_{mix}H^{(i)} - \Delta H_{sol}\frac{n_{En}^{(i)}}{n_{(CuClO_4)_2}^{(i)}} \qquad (8)$$

and $\Delta\alpha_{1,2,3}^{(i)}$ are the fractional changes in the complex ions after the addition of each portion of ethylenediamine (they were obtained by using the stability constants of the complex ions [11]); while $n_{En}^{(i)}$ and $n_{Cu(ClO_4)_2}$ are the quantities (in mol) of ethylenediamine and copper(II) perchlorate in the solution.

The results of the calculations for the monocomplex ($\Delta_r H_1$) are listed in the Table.

Transfer heats of complex ions were obtained according to the following equation:

$$\Delta_t H^0_{[CuEn]^{2+}} = \Delta_t H^0_{Cu^{2+}} + \Delta_t H^0_{En} + \Delta_t H^0_r \qquad (9)$$

resulting from thermodynamic cycle

$$\begin{tikzcd}
Cu^{2+}_{(aq)} \arrow[d, "\Delta_t H^0 Cu^{2+}"] & + & En_{(aq)} \arrow[d, phantom, "\Delta_t H^0 En"] \arrow[r, dashed, "\Delta_r H^0_{(aq)}"] & {[CuEn]^{2+}_{(aq)}} \arrow[d, "\Delta_t H^0 [CuEn]^{2+}"] \\
Cu^{2+}_{(soln)} & + & En_{(soln)} \arrow[r, dashed, "\Delta_r H^0_{(soln)}"] & {[CuEn]^{2+}_{(soln)}}
\end{tikzcd}$$

where:

$$\Delta_t H^0_r = \Delta_r H^0_{(soln)} - \Delta_r H^0_{(aq)} \qquad (10)$$

**Table 1** The enthalphy changes of the reaction of copper(II) mono-complex formation with ethylenediamine in aqueous-organic solvents ( $-\Delta_rH^0$, kJ·mol$^{-1}$)*

| Molar fr. of organic solvent in mixture, ($X_2$) | Mixture | | |
|---|---|---|---|
| | Water–DMSO | Water–Ethanol | Water–Acetone |
| 0.00 | 52.5 | 52.5 | 52.5 |
| 0.10 | 58.6 | 55.8 | 44.5 |
| 0.20 | 61.3 | 59.1 | 41.3 |
| 0.30 | 67.8 | 60.9 | 39.4 |
| 0.40 | 69.8 | 53.4 | 42.5 |
| 0.45 | – | – | 45.0 |
| 0.50 | 72.9 | 48.5 | – |
| 0.70 | 76.6 | 50.6 | – |
| 0.90 | 81.6 | 52.0 | – |
| 0.98 | 89.4 | – | – |

* The $\Delta_rH_i$ values had been taken as standard values of these ones ($\Delta_rH^\circ$), because the ionic strength of the solutions was negligible.

in which $\Delta_rH^0$ (soln) and $\Delta_rH^0$ (aq) are the reaction enthalpies of monocomplex formation in the binary solvent and water, respectively.

## Results and discussion

As shown in Fig. 2, the nature and composition of the aqueous organic solvent influence the thermochemistry of the formation reactions of the ethylenediamine-copper(II) complexes in different ways. In aqueous solutions of dimethylsulfoxide (Fig. 2a), the substitution of solvent molecules in the inner metal coordination sphere by ligand molecules does not exert a significant influence on $\Delta_tH^0$ of the complex ion. This is why the increase in the heat effect of the complex formation reaction ($\Delta_tH^0_r<0$) takes place exclusively because of ligand destabilization in the solution ($\Delta_tH^0_{En}>0$).

In water–ethanol mixtures (Fig. 2b), the inversion of the sign of $\Delta_tH^0_r$ can be observed and these values exceed the changes in $\Delta_tH^0_{En}$ when the mole fraction of ethanol in the solution is about 0.10–0.35. On increase of the dimethylsulfoxide concentration in the solution $\Delta_tH^0_r$ changes insignificantly.

In the aqueous acetone solvent (Fig. 2c), $\Delta_tH^0$ for the reaction is positive (the heat effect of the reaction decreases). This is undoubtedly a result of specific interactions of the ligand and acetone [6]. However, the difference between the transfer enthalpies of the copper(II) and complex ions is large enough, and the value of ($\Delta_tH^0_{[CuEn]^{2+}}-\Delta_tH^0_{Cu^{2+}}$) is negative throughout the whole range of acetone concentrations in the solutions under investigation. This is why the contributions of the $\Delta_t H^0_{En}$ changes to the heat effect of the reaction decrease to a large extent and the value of $\Delta_t H^0_r$ tends towards zero.

These results differ significantly from the corresponding data obtained for nickel(II)-ethylenediamine complexes [1], and indicate the necessity of carrying

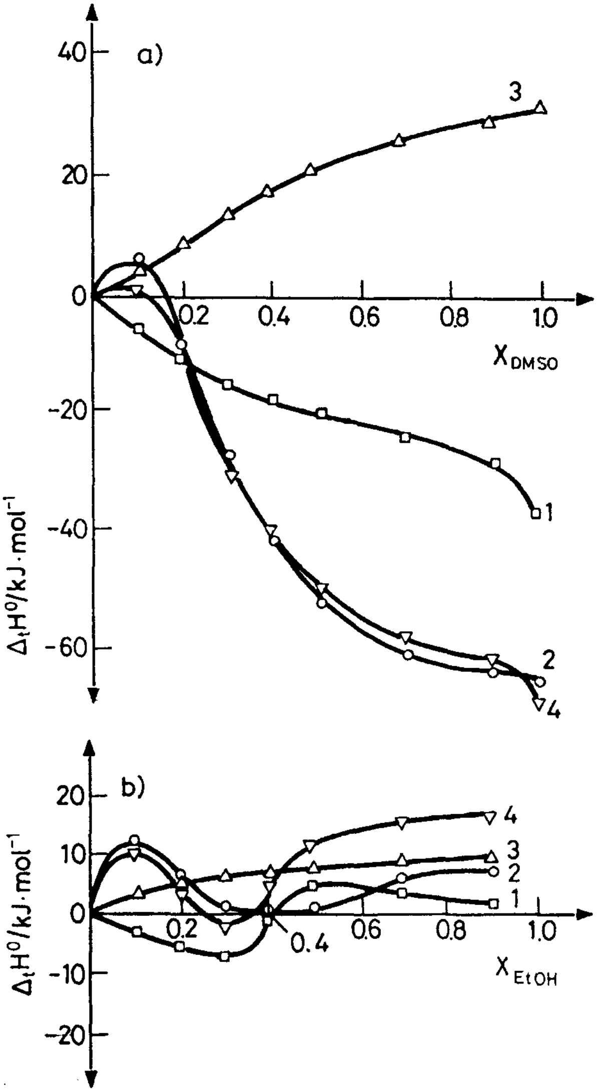

**Fig. 2a,b** Thermochemical analysis of formation of $[CuEn]^{2+}$, based on thermodynamic contributions of reagents: 1. $\Delta_t H^0_r$; 2. $\Delta_t H^0_{Cu^{2+}}$; 3 .$\Delta_t H^0_{En}$; 4. $\Delta_t H^0_{[CuEn]^{2+}}$. Solvents: a) water-DMSO; b) water-ethanol

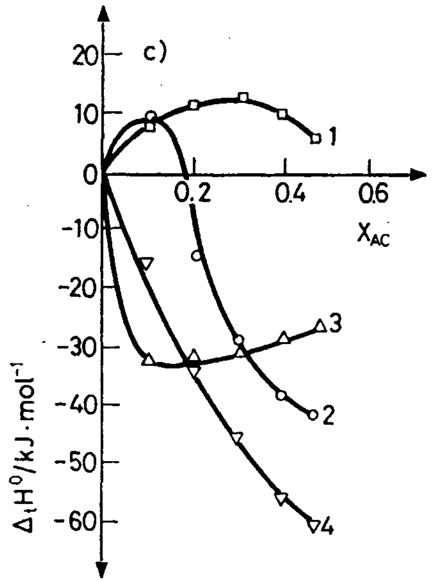

**Fig. 2c** Thermochemical analysis of formation of $[CuEn]^{2+}$, based on thermodynamic contributions of reagents: 1. $\Delta_t H^0_r$; 2. $\Delta_t H^0_{Cu^{2+}}$; 3 .$\Delta_t H^0_{En}$; 4. $\Delta_t H^0_{[CuEn]^{2+}}$. Solvents: water-acetone

out thermochemical investigations of complex formation reactions with other *d*-metals in order to establish the general regularities for the effects of the nature of the solvent on the chemical equilibrium shift and the reaction enthalpy change.

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**Zusammenfassung** — In Gemischen von Wasser mit Ethanol, Aceton und Dimethylsulfoxid wurden die Wärmeeffekte der Bildungsreaktionen von Ethylendiamminkupfer(II)-komplexen kalorimetrisch bestimmt. Die Ergebnisse wurden mit Hilfe der Transferenthalpie ($\Delta_t H^0$) von Komplexbildner, Ligand und Komplexion von Wasser in binäre Lösungsmittel gedeutet.

In einem Wasser-DMSO-Gemisch wurde für die $\Delta_t H^0$ von Cupfer(II) und den Komplexionen eine ähnliche Änderung festgestellt und ihre Beiträge zu den Reaktionswärmeeffekten kompensieren einander in großem Maße. Somit wird die Änderung der Reaktionsenthalpie bei der Änderung der Lösungsmittelzusammensetzung hauptsächlich durch die Änderung der Solvatationsenthalpien der Liganden verursacht.

In wäßriger Lösung von Ethanol und Aceton wird der Wärmeeffekt durch die $\Delta_t H^0$-Änderung aller Reagenzien gleich beeinflußt.