A Calorimetric Study of N,N-Dimethylformamide Complexes of Copper(II) in Acetonitrile

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Complex formation of copper(II) with N,N-dimethylformamide (DMF) has been investigated calorimetrically in acetonitrile at 25°C. Calorimetric titration curves obtained are explained in terms of formation of [Cu(dmf)]_{n}^{2+} (n = 1, 4, 6) and their formation constants, enthalpies and entropies were determined. Formation of [Cu(dmf)]_{5}^{2+} is uncertain. The stepwise enthalpies $\Delta H_n^o$ and entropies $\Delta S_n^o$ at each consecutive step are all negative except for $\Delta S_4^o$. The overall enthalpies of formation of [Cu(dmf)]_{6}^{2+} is -(77.8 \pm 5.4) kJ-mol$^{-1}$, which is compared with the enthalpy of transfer of copper(II) ion, $\Delta H_f^o = -79.7$ kJ-mol$^{-1}$, from acetonitrile to DMF.

KEY WORDS: N,N-Dimethylformamide complexes of copper(II); acetonitrile; calorimetry.

1. INTRODUCTION

Among physicochemical properties of N,N-dimethylformamide (DMF) and acetonitrile (AN), a remarkable difference is seen in their donor properties. The donor number $D_N$ of DMF (26.6) is larger than that of acetonitrile (14.1),(1) which indicates that the former solvent is a better coordinating solvent to metal ions than the latter. Other solvent properties of DMF and acetonitrile are similar [relative dielectric constants $\varepsilon_r$(DMF) = 36.71, $\varepsilon_r$(AN) = 35.95; permanent dipole moments $\mu_o$(DMF) = 12.86$\times$10$^{-30}$ C-m, $\mu_o$(AN) = 13.06$\times$10$^{-30}$ C-m;...

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solubility parameters \( \delta (\text{DMF}) = 11.79 \text{ cal}^\circ/\text{mol}^\circ/\text{cm}^{3/2} \), \( \delta (\text{AN}) = 12.11 \text{ cal}^\circ/\text{mol}^\circ/\text{cm}^{3/2} \); acceptor numbers \( A_N(\text{DMF}) = 16.0, A_N(\text{AN}) = 19.3 \), although boiling and melting points of the solvents are different due to different London interaction energies arising from different molecular weights. Both solvents have such weak intermolecular interactions that they have practically random distributions in the bulk.

Copper(II) ion is more strongly solvated with DMF than with acetonitrile, as indicated by the enthalpy of transfer of the ion from acetonitrile to DMF \( (\Delta H_f^\circ = -79.7 \text{ kJ-mol}^{-1}) \).\(^2\) Therefore, complex formation of a copper(II) with chloride ions proceeds with more negative enthalpies of formation of the complexes in acetonitrile than in DMF.\(^2,3\) The enthalpy values drastically change from negative in pure acetonitrile to positive in acetonitrile rich DMF-acetonitrile mixtures, suggesting the preferential solvation of copper(II) ion with DMF in the mixtures.\(^4\)

In aprotic solvents, the formation of solvation structure of a metal ion is restricted to the first solvation shell because the interactions between solvent molecules in the first and second shells are considered to be very weak.\(^5\) The Gibbs energies of solution of metal ions in mixed solvents were treated theoretically by considering solely the solvation number of metal ions in the first solvation shell.\(^6\) Similarly, the Gibbs energies of transfer of silver(I) ion from various donor solvents to their mixtures with acetonitrile, which strongly solvates the metal ion, were interpreted in terms of the formation of acetonitrile complexes of Ag(I) in the mixtures.\(^7\) Dimethyl sulfoxide complexes of Ag(I) were also reported in various solvents.\(^8\)

These works suggested that the knowledge of complexation of metal ions with one component solvent molecules in mixed solvents is essential to elucidate solvent effects on complex formation equilibria between metal ions and ligands.

In this work, therefore, we calorimetrically studied the complexation of copper(II) ion with \( N,N \)-dimethylformamide (DMF) in acetonitrile as the bulk solvent. The thermodynamic quantities for DMF complexes of Cu(II) thus obtained reflect the solvent effects on the formation of copper(II) chloro-complexes in DMF-acetonitrile mixtures.\(^4\)