Solvation behaviour of copper(II) chloride in some isodielectric media

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Received 22 April 1992; revised 7 September 1992; re-revised and accepted 2 April 1993

Solvation behaviour of copper(II) chloride has been investigated in formamide (FD) or N-methylformamide (NMFD)+1,4-dioxane (D) or N,N-dimethylformamide (DMF) media, isodielectric with water (W) by emf measurements at 303.15 K on the Cu/Hg/CuCl₂ (FD or NMFD+D or DMF)/AgCl/Ag cell. The cell emf which varies as (NMFD+D)<E(FD+D)<E(FD+DMF) has been shown, by graph-theoretical rationalization, to be dictated by the molecular species present in them. The dissociation constant, degree of dissociation of CuCl₂ and the standard cell potentials have also been determined, by iterative procedures, in these media. The molar Gibbs free energy of transfer of CuCl₂ from W→(FD or NMFD+D or DMF) has also been determined and its analysis suggests that it arises, in the present case, due to changes in the interactions of the ions of CuCl₂ in these media.

The solvation of an ion in a solvent involves its transfer from an ideal standard state in the gas phase to its standard state in solution. As the solute particles undergo drastic changes in their degrees of freedom in this process, the thermodynamic quantities of transfer would be a good measure of solute-solvent interactions only if the solute is transferred from one solvent to another solvent. The Gibbs free energy of transfer provides information on chemical interactions from reference solvent to any other solvent if electrostatic contributions are corrected for by Born model. Again very scant information is available about the ionization of MX₂ in isodielectric media. These considerations led us to study the solvation behaviour of copper(II) chloride in formamide (FD)+N,N,N-dimethylformamide (DMF) and formamide (FD) or N-methylformamide (NMFD)+1,4-dioxane (D) media, isodielectric with water at 303.15 K; the choice of lower amides was dictated by the consideration that they are suitable model compounds of proteins and that 1,4-dioxane might be involved in H-bonded interactions with FD.

Materials and Methods

Formamide (BDH, AR grade 98%), N-methylformamide (Fluka >99%) and N,N-dimethylformamide (Loba, AR grade 99%) were purified as described earlier. 1,4-Dioxane (AR grade) was refluxed with sodium metal as suggested by McGlashan and Rastogi, and then fractionally distilled. The purity of the samples was checked as described earlier. All these compounds were stored, over anhydrous CaCl₂ in dessicator, in small amber coloured bottles.

Cupric chloride dihydrate (Loba, AR grade 98%) was dehydrated by heating it in an oven at 130°C for 18 h. Complexometric determination of the copper (II) content of anhydrous CuCl₂ showed that it contained 98.5% of CuCl₂. (FD + D; x = 0.8361), (FD + DMF; x = 0.7020) and (NMFD + D; x = 0.5418) media (where x is the mole fraction of FD or NMFD) isodielectric with W at 303.15 K were prepared by mixing FD or NMFD with D or DMF components by weight, on the assumption that the dielectric constant of the medium is the mole fraction average property of the components of a binary mixture. The necessary dielectric constant data at 303.15 K were taken from the literature.

Required sets of solutions of cupric chloride in each medium, i.e., (FD or NMFD+D) and (FD+DMF) and deionized doubly distilled (from all-glass apparatus) water (W) were prepared by mass dilution of stock solutions prepared from weighed amounts of anhydrous CuCl₂ and solvent; the aqua molality of the stock solution was 0.031 while the molarity of stock solutions of CuCl₂ in (FD+D), (NMFD+D) and (FD+DMF) media were 0.0136, 0.0114 and 0.0158 respectively. All solutions were deaerated with nitrogen. These solutions were subsequently used to measure the emf of the cell.

\[
\text{Cell 1:} \quad \text{Cu, Hg/Cu(II)Cl₂ (m, in w or (FD or NMFD + D) or (FD + DMF)/AgCl/Ag}
\]
The Ag/AgCl electrode was prepared\textsuperscript{10} by anodic polarization of Ag electrode at a current density of 0.4 mA cm\textsuperscript{-2} in 0.1N HCl for 30 min. The copper amalgam was prepared by vigorous shaking of an appropriate amount of freshly prepared atomic copper\textsuperscript{11} with distilled mercury; the percentage of Cu (measured as Cu(II) complexometrically\textsuperscript{9}) in the amalgam was kept below 0.0042\% by suitable manipulation of atomic copper or of distilled mercury. Under these conditions the emf of the copper amalgam electrode was reported\textsuperscript{12} to be independent of the amount of copper in the amalgam.

The cell (1) was maintained at 303.15 ± 0.02 K in a water thermostat and a vernier potentiometer (OSAW, India) coupled with a spot reflecting galvanometer (Toshniwal, India) was used to measure the emf of the cell (1) to an accuracy of ±0.01 mV. The (FD + D or DMF) stock solutions were saturated with analytical grade KCl. A known weight of anhydrous CuCl\textsubscript{2} was then added to these solutions (to yield solutions 7 × 10\textsuperscript{-5} mol dm\textsuperscript{-3} in CuCl\textsubscript{2}) and their DC polarograms were recorded on a Systronic polarograph (Model 62, M/s Systronics, India).

Results and Discussion

We are unaware of any emf (E) data at 303.15 K of CuCl\textsubscript{2} in the present media with which to compare our results. However, while the emf data\textsuperscript{13} at 303.15 K of CuCl\textsubscript{2} in water are negative, they are positive in the present media that are isodielectric with W and vary as (FD + DMF) > (FD + D) > (NMFD + D) > W (Fig. 1) and suggest that there is something in the nature of these media that affects the oxidation of Cu. Again a comparison of the DC polarograms (with and without CuCl\textsubscript{2}) in the same (FD + D or DMF) medium indicated that both the media contain a wave with \(E_{0.5} = -0.31\) V; corresponding\textsuperscript{14} to the electrode process Cu\textsuperscript{2+} \textrightarrow Cu\textsuperscript{0}. The reported\textsuperscript{15} positive \(E_{0.5}\) value in 0.1N KCl (aq) for the electrode process Cu\textsuperscript{2+} \textrightarrow Cu\textsuperscript{0} coupled with the present \(E_{0.5}\) data then suggest that there is something in the nature of the (FD + D or DMF) media that renders the Cu\textsuperscript{2+} \textrightarrow Cu\textsuperscript{0} process difficult in them and so affects the emf data in the present media that are isodielectric with W.

Further if the electron-pair acceptance ability index \(E_{T}\), of the (FD or NMFD + D or DMF) media are taken as the mole fraction average \(E_{T}\) values\textsuperscript{1d} of their constituents, then the \(E_{T}\) values of 63.1, 53.4, 52.8 and 45.4 k cal mol\textsuperscript{-1} for the W, (FD + D), (FD + DMF) and (NMFD + D) media respectively would suggest that not only would Cl\textsuperscript{-} be poorly solvated in the present media than in W [more so in the (NMFD + D) medium than in the (FD + D) medium], the weak solvation of the Cl\textsuperscript{-} in the (NMFD + D) medium would also make the Cl\textsuperscript{-} very active in complexing the cations in this medium. This would then require that while the emf data of cell 1 with CuCl\textsubscript{2} in the (FD + D or DMF) media should be of almost the same magnitude, it should not only differ appreciably from the corresponding emf data in the W and the (NMFD + D) medium but should also decrease with an increase in the concentration of CuCl\textsubscript{2} in the latter medium. This is indeed true of the present emf data (Fig. 1). The present emf data then reflects the tendency of the Cl\textsuperscript{-} to complex with the cations in these media.

To substantiate these conclusions we next investigated the extent of dissociation of CuCl\textsubscript{2} in the present media, utilizing the relevant emf data in the manner suggested by Hefley and Amis\textsuperscript{16}. The nonlinear \(E^{\alpha}[E^{\alpha} = E + RT/2F \ln 4m^{3/2}(3RT/2F) \times A_{9/2}m = E_{0} - \alpha m\) (where \(X = (6.909/2F)RTB\)) versus \(m\) plots (Fig. 2) clearly suggest that CuCl\textsubscript{2}...
is incompletely dissociated in water and the present isodielectric media.

If CuCl$_2$ ionizes in these media as

$$K_1$$

\[
\text{CuCl}_2 \rightleftharpoons (\text{CuCl})^+ + \text{Cl}^- 
\]  

and if $\alpha_1$ and $\alpha_2$ are the degree of dissociation of CuCl$_2$ and (CuCl)$^+$, respectively, with equilibrium constants $K_1$ and $K_2$ then

$$\alpha_1 = 0.5 \left[ -P + (P^2 + 4P)^{0.5} \right]$$

where

$$P = K_i / m \gamma_{Cl^-} \left( 1 - \alpha_2^2 \right)$$

$$Q = K_j / \alpha_1 m \gamma_{Cu^{+}}$$

In deriving Eqs 3 and 4 it has been assumed$^{16,17}$ that $\gamma_{Cl^-} = \gamma_{CuCl_2}$, and $\gamma_{Cu^{+}}$ is the real activity coefficient of Cu$^{2+}$ ion with actual concentration. This would then mean$^{16}$ that $\gamma_{Cu^{+}}$ and $\gamma_{Cl^-}$ should have values$^{17}$ comparable to those found for a typical strong electrolyte and should be expressible in a medium of dielectric constant $\epsilon$ and at an actual ionic strength $I$ by

$$\log \gamma_i = \frac{-A \epsilon \alpha_i^3/(1 + \alpha_i^3) + B \epsilon I}{2F}$$

where $Z_i$ represents the valency of Cu$^{2+}$ or Cl$^-$ ion, and

$$\epsilon = \frac{1.823 \times 10^6}{(\epsilon T)^{0.5}}$$

$$B = 35.56 \text{ a}^{0.9}/(\epsilon T)^{0.5}$$

where $a^0$ is the distance of closest approach of the ions of electrolyte in $A^*$ and which for 2:1 electrolyte has been taken$^{17}$ to be $5A^*$. The measured emf ($E$) of the cell I would then be related$^{16}$ to the standard cell potential $E^0$ by

$$E' = E + \frac{2.3026RT}{2F} \left[ \log \left( \alpha_2 \alpha_1^2 \right) + \frac{3A \epsilon \alpha_1^3}{(1 + \alpha_1^3)} \right]$$

where $I_1 = \alpha_1 (1 + 2 \alpha_2) m$

and it being assumed$^{17}$ that

$$\log \gamma_i = \frac{-A' \epsilon \alpha_i^3/(1 + \alpha_i^3) + B \epsilon I}{2F}$$

where

$$A' = \nu^{-1} (\Sigma v_i Z_i^2) \times 1.29 \times 10^6/(\epsilon T)^{0.5}$$

Iterative procedures$^{17c,18}$ were next employed to evaluate $K_1$, $K_2$, $\alpha_1$, $\alpha_2$ and $E^0$ data from Eq. 10. Such data are recorded in Table 1 and a perusal of $K_1$ and $K_2$ data has revealed that while $K_1$

<table>
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<tr>
<th>$m$</th>
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Table 1—Measured cell emf $E$ (in volt) as function of the molality $m$ of CuCl$_2$ along with the equilibrium constants of the equilibria 1-2, standard cell potential $E^0$, mean molar activity coefficient $\gamma_{Cu^{+}}$, degree of dissociation $\alpha_1$, and $\alpha_2$, regression coefficient $r$ and the slope $s$ of the LHS of Eq. 10 versus $I$ at 303.15 K. Also included are the $\Delta G^o(tr)$ (CuCl$_2$, $W^-S^-$, $S^--(FD+D$ or DMF) data

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$K_1 = 0.001; K_2 = 0.00001; r = 0.9441; s = -7.6740; E^0 = -0.0524 V; \Delta G^o(tr) (CuCl_2, W^-S^-; S^-)(FD+D or DMF) = -78.3 kJ mol$ $^{-1}; E^* = 0.3985 V$ (ref. 13).
is the same in all these media, $K_2 (NMFD + D) > K_2 (FD + D \text{ or } DMF)$ or W. This suggests that there must be something in the nature of these solvents media that influences equilibrium 2 to that extent. An ion is modified by and modifies the solvent structure. The excess Gibbs free energy and excess enthalpy data of (CHCl$_3$ + D) mixtures at 323.15 K, and the existence of maxima in the viscosity and ultrasonic velocity data of (W + DMF) mixtures have been shown$^{7,20,21}$ to be dependent on the presence of molecular species in them. Hence an investigation of the present solvent media might give worthwhile information about the probable molecular species (and of their role in influencing equilibrium 2) in them.

For this purpose we carried out graph theoretical analysis$^{22,23}$ of the $V^e$ data$^{24}$ of the (FD + D or DMF) and (NMFD + D) mixtures and it suggested that while D in the pure state should exist as I, FD should exist as II or as III and DMF should exist as IV or as an equilibrium mixture of IV and IV(a) if chain structures exist$^{19b}$ in DMF (which is not associated through H-bonds); it being assumed that the CH$_3$ vertices of DMF are influenced in IV(a) formation. NMFD was similarly indicated to exist in the pure state as an equilibrium mixture of V and VI. The present analysis while supporting Davies$^{25}$ views about the state of aggregation in the lower amides in the liquid state further suggested that the (FD + D) medium should contain an equilibrium mixture of VII (or VIII) and III provided the C vertices of D are not influenced in the (FD + D) mixture formation. The infrared spectrum of the (FD + D; 1:1 mixture) [with absorptions at 3380-3300, 2940 (new band), 2835 and 1125 cm$^{-1}$] supported it. Again the presence of 2 pairs of electrons on each of the two oxygen atoms of D would require that the (FD + D) mixture should contain at least 1:1 and 1:2 molecular entities. The [FD(A) + DMF(B)], mixture was further suggested to contain IX (on the assumption that the vertices in the dotted line are influenced by H-bonded interaction between FD and DMF) along with IV and the [NMFD(A) + D(B)] mixture was similarly deduced to contain the entity XII.

Further as the present (FD + D) medium contained 84 mole per cent of FD, while the (FD + DMF) and the (NMFD + D) media contained 70 and 52 mole per cent respectively of FD and NMFD, the above arguments would envisage that while the (FD + D) medium should contain predominantly VII (and or VIII), the (FD + DMF) medium should contain IX and IV and the (NMFD + D) medium should contain XII. the presence of a CH$_3$ substituent on the N atom in XII would evidently increase the lone pair donating ability of the carbonyl oxygen atom of XII (as compared to that of VII (and VIII) and IX) towards the Cu$^{2+}$ ion. This would then require that the equilibrium 2 be shifted considerably to the right in the (NMFD + D) medium than in the (FD + D or DMF) media. The $K_2 (NMFD + D)$ or W lends credence to this viewpoint. Again the greater lone pair donating ability of the N atom of XII would also not only cause Cu$^{2+}$ to undergo the Cu$^{2+} + 2e^- \rightarrow Cu^0$ process more favourably in the solvating sheath of the (NMFD + D) medium than that in the (FD + D or DMF) media, but would also render the Cl$^-$ to be poorly solvated in the former medium than that in the latter media. The above arguments would then require that the ability of Cl$^-$ to complex with Cu$^{2+}$ in the present media should vary as (NMFD + D) > (FD + D) > (FD + DMF). This lends additional support to the $E^\circ$ data $[E^\circ(NMFD + D) > E^\circ(FD + D) > E^\circ(FD + DMF)]$ obtained by the present iterative method. The present emf data should vary as $E(FD + DMF) > E(FD + D) > E(NMFD + D)$. This is indeed the case.

The $E^\circ$ data in the present media were next coupled with the $E^\circ = 0.3985$ V value$^{13}$ in W at 303.15 K to evaluate molar Gibbs free energy of transfer of CuCl$_2$ from W to the isodielectric (FD or NMFD + D or DMF) media utilizing the relationship$^{26}$.

\[\text{Equation}\]
\[ \Delta G^\circ (tr) [\text{CuCl}_2, W \to S', S'] = \begin{cases} \text{(FD or NMFD + D or DMF)} & = -2F[E^\circ_S - E^\circ_W] \\ -3RT \ln \left( \frac{M_{S'}}{M_w} \right) \end{cases} \] ...

... (11)

where \( M_S \) is the molar mass of the solvent \( S' \).

Such \( \Delta G^\circ (tr) \) data in Table 1 suggest that the transfer of \( \text{CuCl}_2 \) from \( W \) to the isodielectric present media is energetically favourable; more so in the (NMFD + D) medium than in the (FD + DMF) medium. This is as it should be; the poorer solvation of \( \text{Cl}^- \) in the (NMFD + D) medium than in the (FD + D or DMF) medium would actually require it to be so. Again as the transfer of an electrolyte from one medium to another involves the transfer of the charged species, the \( \Delta G^\circ (tr) \) data must involve contributions due to (i) changes in the dielectric constant of the medium (i.e. \( \Delta G^\circ (tr) \) (electrostatic)) and (ii) cation-solvent and anion-solvent interactions (i.e. \( \Delta G^\circ (tr) \) (Chem)).

Following Roy et al., \( \Delta G^\circ (tr) [\text{CuCl}_2, W \to S'] \) may then be expressed as \( \Delta G^\circ (tr) [\text{CuCl}_2, W \to S'] = [\Delta G^\circ (tr) \) (electrostatic) + \( G^\circ (tr) \) (Chem)].

If the electrostatic component of \( \Delta G^\circ (tr) [\text{CuCl}_2, W \to S'] \) is assumed to be well described by the Born-model\(^3\) of ion-solvation, then the \( \Delta G^\circ (tr) [\text{CuCl}_2, W \to S'] \) values in the present case should arise due to changes in the interactions of ions of the electrolyte in the present solvent media; as has been shown in the earlier paragraph.

The present study thus has revealed that the nature of molecular entities play a very important role in influencing ion-ion interactions and hence emf data in isodielectric media.

Acknowledgement

One of the authors (M S) thanks the UGC, New Delhi for providing financial assistance.

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