Association of Cu(NO₃)₂ with Kryptofix-221 in Mixed (MeOH-DMF) Solvents at Different Temperatures

E. A. Gomaa*, B. M. Al-Jahdali
Chemistry Department, Faculty of Science, Mansoura University, Mansoura, 35516, Egypt

Abstract
New equation was applied for the calculation of association constant (KA) from the reaction of Cu(NO₃)₂ with Kryptofix-221 in mixed (MeOH-DMF) and in absence and presence of ligand at different temperatures. From the experimental results, the molar conductance (Λ) were evaluated. The limiting molar conductance (Λ₀) were also estimated. Gibbs free energies of association (ΔGₐ) was also estimated, Moreover, recalculation of (Kₐ) was achieved by applying Shedlovsky and Fouss-Kraus extrapolation methods. In addition, the molar solvated (Vₐ), Van der Waals (V₊), electrostriction (Ve) and apparent molar (Vo) volumes were calculated. Also, the enthalpy change (ΔH) and the entropy change (TΔS) for Cu(NO₃)₂ were calculated. The degree of dissociation (α) were also calculated. All the results were discussed in view of ion-solvent interactions.

Keywords
Association, Kryptofix-221-Dissociation, Molar Solvated Volume, Van der Waals Volume, Electrostriction Volume, Free Energy of Association, Denisties, Molar Fraction, Limiting Conductance

1. Introduction
Although metal cations play an important role both in chemistry and biology, the coordination chemistry of metals was completely ignored by chemists. However, the coordination chemistry of metal cations has mainly developed by the synthesis of crowns by Pedersen[Pedersen, (1967)][1]. The discovery of the crown ethers was followed by synthesis of macro bicyclic poly ethers containing three poly ether strands joined by two bridge head nitrogens[Lehn et al., (1971)][2].

These compounds have three-dimentional cavites which can accommodate a metal ion of a suitable size and from an inclusion complex.

These ligands which developed by Lehn and his co-workers [Dietrich et al., (1969)][3], were called[2] – Cryptands where[2] indicates the bicyclic ligand such as Kryptofix-221 which its structure is given in Fig (1). The crown compounds and their thia – and aza – derivatives have a considerable interest in terms of their complexation properties in solution with univalent and bivalent metals[Gokel, (1976)][4]. It is important to mention that the marocyclic crown ethers have many applications[Izatt et al., (1978)][5] in biological activity, corrosion chemistry, analytical chemistry, phase – transfer catalysis and industrial production such as nuclear energy, electronics and electro–chemical photosensitive materials[El-Dossouki; (1998)][6]. On understanding the interactions between macrocyclic crown ethers such as Kryptofix-221 and metal cations in solutions, it requires the study of various parameters govering these interactions. The thermodynamic studies of these interactions gave important informations about their complexation reactions and the selectivities of these ligands towards different metal cations[Rounaghi et al., (1999)][7]. The ab-served association constant values are known to be a composite quantities depending on specific and non-specific solute – solvent interactions. The separation of various interaction contributions is often very difficult process, beside that using mixed solvents it add another dimention to the problem[Mukhopadhyay et al., (1997)][8]. The multitdentate macro molecules (MMM) which have been studied as ligands for M²⁺ were included natural antibiotics and synthetic compounds such as crowns and cyptands[9]. The macro molecular ligands had recently become more important to the chemistry of M²⁺ than the conventional ligands, this was because they binded M²⁺effectively and rendered the latter soluble in non-polar solvents and because they were more relevant to the chemisrty of M²⁺ in biological system which thereinvolved essentially the macrobi-o-molecules.

A conductance study of the interaction between Co³⁺, Ni²⁺, Cu²⁺, Cd²⁺, Zn²⁺ and pb²⁺ ions with Kryptofix-221, K-22& K-222 in different (acetonitrile-dimethyl sulfoxide) mixtures was carried out at various temperatures by Shamsipur[10]. The aim of the present work is to study the conductivity of Cu(NO₃)₂ in the absence and in presence of Kryptofix-221 using different molar ratios of (MeOH-DMF) mixed solvents
at different temperatures. By applying Shedlovsky-Fouss-Kraus extrapolations[11] methods, we were able to evaluate the values of \((\Lambda_0), (K_A), (\Delta G_A)\) and to make an acceptable discussion.

Finally, the crystal and molecular structures of about 200 metal halide complexes with oxygen–Containing crown ethers were investigated by Bel'sky[12]. The characteristic features of the formations of these complexes and their coordination fragments were discussed.

Figure 1. Kryptofix-221 [4,7,13,16,21-pentaoxa-1,10-diazo-bicyclo[8,8,5]tricosane]

2. Experimental

The aza-crown ether, Kryptofix-221[4.7.13.16.21-pentaoxa-1-diazo-bicyclo[8,8,5]tricosane] was supplied from Merck Co. whereas, copper nitrate Cu(NO\(_3\))\(_2\) of high grade was supplied from BDH and it was used without any further purification.

The water content of the salt was determined by using (Mettler DI-18) Karl-Fisher titrator and it was found to be less than \(\pm 0.01\%\).

All solvents used MeOH&DMF were BDH supplements used without any further purification.

The measurements of the specific conductance of Cu(NO\(_3\))\(_2\) in the presence of Kryptofix-221 in all the mixed (MeOH - DMF) solvents were achieved at different temperatures using Beckman Conductivity Bridge Model No. (RE – 18A).

All the conductometric titrations were done using 1x10\(^{-3}\) mol./lit. Cu (NO\(_3\))\(_2\) and 1x10\(^{-4}\) mol. /lit. of 332, 44 gm/mol, Kryptofix-221.

Spectrophotometrical continuous variation study of Cu(NO\(_3\))\(_2\) in the presence of Kryptofix-221 at different temperatures and in 20% MeOH was achieved using Unicam UV-2-100 UV/Visible spectrometer \(\lambda\) 3.32; at wave length of \(\lambda\) max (284nm).

3. Results and Discussion

The specific conductance values \((K_s)\) of different concentrations of Cu(NO\(_3\))\(_2\) in (MeOH-DMF) mixtures in the absence and in the presence of Kryptofix-221, were measured experimentally and from which the values of molar conductance \((\Lambda)\) were calculated [Walter, (1976)] by using

\[
\Lambda = \frac{(K_s - K_{mol})K_{cell} \times 1000}{c} \quad (1)
\]

Where \((K_s)\) and \((K_{solv})\) are the specific conductances of the solution and the solvent, respectively; \((K_{cell})\) is the cell constant and \((c)\) is the molar concentration of Cu (NO\(_3\))\(_2\).

The association constant value \((K_A)\) of different concentrations of Cu (NO\(_3\))\(_2\) in (MeOH - DMF) mixtures in the presence and in the absence of Kryptofix-221, were calculated by using eq.(2)

\[
A^{2+} + 2B^- \rightleftharpoons AB_2
\]

\[
K_A = \frac{1 - \alpha}{4c(\gamma \pm \alpha)^2}
\]

From, \(\alpha = \frac{\Delta s(z)}{\Lambda_0}\)

Where (\(\Lambda\)) is the molar conductance, \((\Lambda_0)\) is the limiting molar conductance.

\[
K_A = \frac{\Lambda_0^2(\Lambda - \Lambda_0)}{4c(\gamma \pm \alpha)^2 \Lambda s(z)} \quad (2)
\]

Where (\(\alpha\)) is the degree of dissociation, Fuoss-Shedlovsky parameters (S, Z and s(z), activity coefficient (\(\gamma_+\)) association constant (\(K_A\)).

The evaluations of Gibbs free energies of association \((\Delta G_A)\) for Cu(NO\(_3\))\(_2\) with Kryptofix-221 in (MeOH -DMF) mixtures at different temperatures, were gained according to eq.(3).

[Kappenstein, (1974)]\[13\].

\[
\Delta G_A = -2.303 RT \log K_A \quad (3)
\]

\[
\Delta G_A = \Delta H_A - T \Delta S_A
\]

From the densities measurements of solvents (MeOH-DMF) and the densities of Cu (NO\(_3\))\(_2\) at different temperatures, the molar volumes \((V)\) were calculated and their values are listed in Table (1). The packing density \((P)\) as reported by Kim and Gomaa[14], i.e, the relation between Vander Waals volume \((V_W)\) and the molar volume \((V)\) as shown in the following eq. (4).

\[
P = \frac{V_W}{V} = 0.661 \pm 0.017 \quad (4)
\]

The electrostriction volume \((V_e)\), which is the volume compressed by the solvent can be calculated by using eq (5) as following:

\[
V_e = (V_W - V) \quad (5)
\]

The apparent molar volumes \((\phi_m)\) were also calculated by the following eq. (6)[15].

\[
\phi_m = \frac{M_2}{m_d - 1000} (d - d_0)/(m_d \cdot d_0) \quad (6)
\]

Where, \((M_2)\) is the M.Wt of DMF, \((d_0)\) is the density of the solvent and \((m)\) is the molality .

The values of the solvated radius \((r_s)\) were calculated by using eq. (7) [(Gomaa, (16)]

\[
V = N \pi r_s^3 / 6 \quad (7)
\]

\[
r_s = \frac{\sigma}{2}
\]
Table 1. The molar volume ($V_v$), solvated Vander Waals ($V_w$) and electrostriction volumes ($V_e$) of Cu(NO$_3$)$_2$ in (MeOH-DMF) mixtures at different temperatures

| Vol% MeOH | $V_v$(cm$^3$.mol.$^{-1}$) | $V_w$(cm$^3$.mol.$^{-1}$) | $V_e$(cm$^3$.mol.$^{-1}$) |
|----------|---------------------|---------------------|---------------------|
| 0        | 298.15K             | 303.15K             | 313.15K             |
| 20       | 77.20               | 77.81               | 77.90               |
| 40       | 55.45               | 55.88               | 56.07               |
| 100      | 40.76               | 41.16               | 41.26               |

Table 2. The apparent molar volumes ( $\varphi'$), the solvated radius($r$), and the apparent molar volume at infinite dilution ( $\varphi''$) of Cu(NO$_3$)$_2$ in (MeOH – DMF) mixtures at different temperatures

| Vol% MeOH | $\varphi'_{\times 10^3}$ | $r_{\times 10^{-5}}$ | $\varphi''$ |
|-----------|--------------------------|----------------------|------------|
| 0         | 298.15K                  | 303.15K              | 313.15K    |
| 20        | -7.84                    | 18.67                | -30.63     |
| 40        | 19.61                    | 28.33                | -10.82     |
| 100       | 30.24                    | 68.76                | -16.94     |

Table 3. The values of $\Lambda$, $\Lambda_\alpha$, $\gamma \pm$, $\alpha$, $K_s$ and $\Delta G$ of Cu(NO$_3$)$_2$ in mixed (MeOH–DMF) solvents at different temperatures using Fuoss–Shelodovsky method

| Vol% MeOH | $C_m \times 10^4$ | $\Lambda$ | $\Lambda_\alpha$ | $\gamma \pm$ | $\alpha$ | S(z) | $K_s \times 10^5$ | $\Delta G$ |
|-----------|------------------|----------|------------------|-------------|--------|-----|-----------------|-----------|
| 0         | 298.15K          | 303.15K  | 308.15K          | 313.15K     |        |     |                 |            |
| 20        | 8.0              | 154.1    | 175              | 9.4386      | 0.882  | 1.0 | 7.52            | 39.25     |
| 40        | 8.0              | 149.1    | 170              | 9.3612      | 0.878  | 1.0 | 7.95            | 39.39     |
| 100       | 8.0              | 158.8    | 180              | 9.2948      | 0.882  | 1.0 | 7.77            | 39.34     |

Table 4. The Values of $\Lambda$, $\Lambda_\alpha$, $\gamma \pm$, $S(z)$, $\alpha$, $K_s$ and $\Delta G$ of Cu(NO$_3$)$_2$ in presence of Kryptofix-221 and in (MeOH-DMF) mixtures, at different temperatures using Fuoss–Shelodovsky method

| Vol% MeOH | $C_m \times 10^4$ | $\Lambda$ | $\Lambda_\alpha$ | $\gamma \pm$ | $S(z)$ | $\alpha$ | $K_s \times 10^5$ | $\Delta G$ |
|-----------|------------------|----------|------------------|-------------|--------|--------|-----------------|-----------|
| 0         | 298.15K          | 303.15K  | 308.15K          | 313.15K     |        |       |                 |            |
| 20        | 8.0              | 658.5    | 760              | 0.9418      | 1.0066 | 0.872 | 9.008           | 39.702    |
| 40        | 8.0              | 875      | 780              | 0.9436      | 1.0    | 0.865 | 9.11            | 40.39     |
| 100       | 8.0              | 467.5    | 740              | 0.9382      | 1.0    | 0.631 | 64.66           | 45.34     |
Where \( \Delta \) is the diameter, the evaluated data are given in Tables (3), (4).

The experimental conductometric data of the equivalent measurements of Cu(NO₃)₂ in mixed solvents were analyzed using Shedlovsky and Fuoss – Kraus extrapolation techniques which have been mentioned earlier in Dash’s publication[17] as given.

\[
\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_o} + \frac{K_A}{\Lambda_o} \left[ C \cdot \Lambda \cdot \gamma^2 S(z) \right]
\]

(8)

Where \( S(z) = 1 + Z + Z^2/2 + Z^3 /3 + \text{etc} \)

\[
\left( Z \right) = \frac{S(C)^{1/2}}{\Lambda^{3/2}}
\]

(9)

Where \( S = a \cdot \Lambda_o + b, a = \frac{8.2 \times 10^5}{(\Lambda \cdot \epsilon \cdot T)^{3/2}}, b = \frac{0.825}{\eta_o \cdot (\epsilon \cdot T)^{1/2}} \)

\[
\log \gamma_{\pm} = -\Lambda S(z) / \Lambda_o
\]

(10)

Where \( (A) \) and \( (B) \) are the Debye-Huckel constants, \( (r^* \) is the ion size parameter, \( (\eta_o \) and \( (\epsilon \) are the viscosity and the dielectric constants of the MeOH-DMF mixed solvent, respectively. All the parameters calculated by Shedlovsky method at different temperatures are given in Tables (3), (4).

Table (5) (a,b,c), illustrated the thermodynamic parameters \( (\eta_o \Delta G_o), (\Delta H_o) \) and \( (\Delta S) \) of the solvation of Cu(NO₃)₂ with (MeOH - DMF) in presence and absence of Kryptofix-221.

All their values were calculated from the solubilities measurements. The \( (\Delta G_o) \) values found to be increased by increasing the content of the organic solvent (MeOH-DMF) mixtures.

On the other hand, the values of \( (\Delta H_o) \) and \( (\Delta S) \), were generally found to be decreased by increasing the methanol content in the mixtures used.

It was concluded from Table (6), that, the association constant \( (K_A) \) of Cu(NO₃)₂ in presence and absence of Kryptofix-221 in (MeOH – DMF) mixtures, at different temperatures, using the different methods [Fuoss – Shedlovsky and Fuoss- Kraus] have nearly the same values.

This indicates that, the association constants in this case are due to the formation of different stiochiometric complexes as mentioned in this table. The formation of these complexes are probably be outside the Kryptofix ring.

The graphical presentation of the relation between \( \log K_A \) and the inverse temperatures \( \left( \frac{1}{T} \right) \) at different temperatures, give slope and from their slopes, we can calculate the thermodynamic parameters \( (\Delta H_A) \).

Also, we plot the relation between \( \log \Lambda_o \) and \( \left( \frac{1}{T} \right) \) in presence and absence of Kryptofix-221.

The graphical presentation of the relation between the association free energies \( (\Delta G_A) \) and the mole fraction \( (X_s) \) of the organic solvent used at different temperatures at four different mole fraction of Cu(NO₃)₂ and Kryptofix-221 are show in .

Also the graphical presentation of the relation between the apparent molar volume \( (\varphi_s) \) and \( (\sqrt{S(z)}) \), where \( (\sqrt{S(z)}) \) in the molality shown in .

4. Conclusions

It was concluded that, the \( K_A \) association of metal cation with Kryptofix increase with increase of temperatures and also, with increase of the methanol content in the mixtures due to the increase of ion-ion and ion-solvent interactions. KA values increased by increase methanol content in the mixed solvents due to the preferential slovation of copper with methanol than the mixed solvent and dimethyl formamide. \( K_A \) values increase also by increasing temperatures due mainly to the increase in kinetic energy and kinetic work necessary to do salvation process. \( \log K_A \) values calculated by different methods indicate that the values are small in case of Fuoss and Fuoss-Kraus methods in comparison to that values which have calculated. Therefore our values are near to the true picture of the greater ions. It was also concluded that the free energies of complexation increase with increase in methanol content due to the increase of interaction of the divalent metal cation with Kryptofix-221. According to the too low concentration used, the entropy parameter show no significant rule in this work.
Table 5. The values of $\Delta G$, $\Delta H$ and $T \Delta S$ of Cu(NO$_3$)$_2$ in mixed (MeOH-DMF) solvents in presence and absence of Kryptofix-221 at different temperatures.

| Vol% MeOH | $\Delta G_a \times 10^4$ (J.mol$^{-1}$) | $\Delta G_c \times 10^4$ (J.mol$^{-1}$) | $\Delta H_c \times 10^4$ (J.mol$^{-1}$) | $\Delta H, X 10^4$ (J.mol$^{-1}$) |
|-----------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
|           | 298.15k                          | 303.15k                          | 308.15k                          | 313.15k                          |
| 0         | -39.7                            | -40.39                           | -41.69                           | -42.43                           |
| 20        | -39.89                           | -43.87                           | -44.21                           | -46.69                           |
| 40        | -39.86                           | -42.76                           | -43.34                           | -42.61                           |
| 100       | -40.09                           | -45.34                           | -45.46                           | -42.94                           |

Table 6. The values $\log K_a$ of Cu(NO$_3$)$_2$ in presence of Kryptofix-221 and in (MeOH-DMF) at different temperatures using different methods.

| Vol% MeOH | $\log K_a$ complex | $\log K_a$ F-shedlovesky | $\log K_a$ F-kraus |
|-----------|--------------------|--------------------------|---------------------|
| 298.15K   | 303.15k            | 308.15k                  | 313.15k             |
| 0         | 6.95               | 6.96                     | 7.06                |
| 20        | 6.98               | 7.55                     | 7.49                |
| 40        | 6.98               | 7.36                     | 7.35                |
| 100       | 7.02               | 7.8                      | 7.7                 |

REFERENCES

[1] Pedersen C.J. (1967) Am. Chem. SoC.89,7017
[2] Lehn J.M.; Sauvage J.P. (1971) Chem. Comm., 440
[3] Dietrich B.; Lehn J.M. and Sauvage J.P. (1969) Tetrahedran Lett., 2885& 2889
[4] Gokel G. W.; Durst H.D. (1976) Synthesis, 168
[5] Izatt R.M.; Izatt N.E.; Rossiter B.E.; Christensen J.J. and Haymore B.L. (1978) Science 199,994
[6] El-Dossouki F.I. (1998) Ph.D. Thesis; Mansoura University; Egypt
[7] Rouanhi G.; Nejad F.M. and Taheri K. (1999) Ind. J.Chem. 38A, 568
[8] Mukhopadhyay A.; Chattopadhyay M.R. and Pal M. (1997) Ind. J.Chem. 36A, 94
[9] Poonia N.S.; Bajai A.V, Coordination Chemistry of Alkaline and Alkali Earth Cations, Chem. Rev, 79, (1979), 389
[10] Shamsipur M.; Ghasem; J, J Inclusion Phenom Mol Recognit Chem, 20(2), (1995), 157
[11] Fouss R.M.; Edelson D. (1951) J.Am.Chem.Soc.73,269
[12] Bel'sky K.V., Chem Rev, 68(2), (1999). 119
[13] Kappenstein C. (1974) Bull. Soc.Chim. Fr. 89,101
[14] Kim J.I, Zeitschrift Fur Physikalische Chemie Neue Folge, 110, (1978), 197and Gomaa E.A.Thermochim.Acta ,152 (198) 371
[15] Gryblavwski W.; Pastewslai Electro Chimice Acta, 25(1980) 279
[16] Gomaa E.A., Therm.Chim. Acta, 152 (1989) 71
[17] Dash N.U.; Pasupalak N.N, Ind. J.Chem, 36(A), (1997) 88

K$_a$ in (mol/L)