

Association of $\text{Cu}(\text{NO}_3)_2$ with Kryptofix-221 in Mixed (MeOH-DMF) Solvents at Different Temperatures

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Abstract New equation was applied for the Calculation of association constant (K_A) from the reaction of $\text{Cu}(\text{NO}_3)_2$ 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 (Λ_0) were also estimated. Gibbs free energies of association (ΔG_A) was also estimated, Moreover, recalculation of (K_A) was achieved by applying Shedlovsky and Fouss-Kraus extrapolation methods. In addition, the molar solvated (V), Van der Waals (V_w), electrostriction (V_e) and apparent molar (ϕ_v) volmes were calculated. Also, the enthalpy change (ΔH) and the entropy change ($T\Delta S$) for $\text{Cu}(\text{NO}_3)_2$ 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-dimensional cavities which can accommodate a metal ion of a suitable size and form 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 macrocyclic 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 governing these interactions. The thermodynamic studies of these interactions gave important information about their complexation reactions and the selectivities of these ligands towards different metal cations [Rounaghi et al., (1999)] [7]. The observed association constant values are known to be a composite quantity depending on specific and non-specific solute – solvent interactions. The separation of various interaction contributions is often a very difficult process, beside that using mixed solvents it adds another dimension to the problem [Mukhopadhyay et al., (1997)] [8]. The multidentate macro molecules (MMM) which have been studied as ligands for M^{z+} were included natural antibiotics and synthetic compounds such as crowns and cryptands [9]. The macro molecular ligands had recently become more important to the chemistry of M^{z+} than the conventional ligands, this was because they bind M^{z+} effectively and rendered the latter soluble in non-polar solvents and because they were more relevant to the chemistry of M^{z+} in biological systems which there involved essentially the macrobiomolecules.

A conductance study of the interaction between Co^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} and Pb^{2+} 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 $\text{Cu}(\text{NO}_3)_2$ in the absence and in presence of Kryptofix-221 using different molar ratios of (MeOH-DMF) mixed solvents

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at different temperatures. By applying Shedlovsky, Fuoss-Kraus extrapolations [11] methods, we were able to evaluate the values of (Λ_o), (K_A), (ΔG_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.

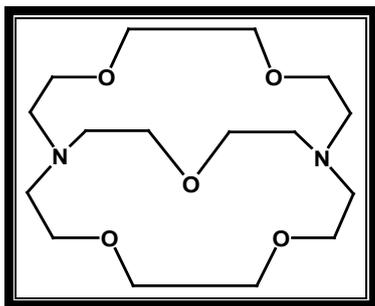


Figure 1. Kryptofix- 221 [4,7,13,16,21- pentaoxa-1.10-diazo-bicyclo [8,8,5] tricosane]

2. Experimental

The aza-crown ether, Krypto fix-221 [4.7.13.16.21-pantaoxa - 1.10 - diazo bicyclo [8.8.5] tricosane) was supplied from Merck Co. where as, copper nitrate $\text{Cu}(\text{NO}_3)_2$ 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 conductivity of $\text{Cu}(\text{NO}_3)_2$ 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 1×10^{-3} mol./lit. $\text{Cu}(\text{NO}_3)_2$ and 1×10^{-4} mol. /lit. of 332, 44 gm/mol, Kryptofix-221.

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

3. Results and Discussion

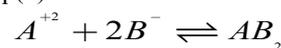
The specific conductance values (K_s) of different concentrations of $\text{Cu}(\text{NO}_3)_2$ in (MeOH-DMF) mixtures in the absence and in the presence of Kryptofix-221, were measured experimentally and from which the values of molar conductance (Λ) were calculated [Walter, (1976)] by using

eq. (1):

$$\Lambda = \frac{(K_s - K_{\text{solv}})K_{\text{cell}} \times 1000}{c} \quad (1)$$

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 $\text{Cu}(\text{NO}_3)_2$.

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



$$K_A = \frac{1 - \alpha}{4cm^2 \gamma_{\pm}^2 \alpha^3}$$

$$\text{From, } \alpha = \frac{\Lambda s(z)}{\Lambda_o}$$

Where (Λ) is the molar conductance, (Λ_o) is the limiting molar conductance.

$$K_A = \frac{\Lambda_o^2 (\Lambda_o - \Lambda)}{4cm^2 \gamma_{\pm}^2 \Lambda^3 s(z)} \quad (2)$$

Where (α) is the degree of dissociation, Fuoss-Shedlovsky parameters (S , Z and $s(z)$, activity coefficient (γ_{\pm}) association constant (K_A).

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

[Kapenstein, (1974)] [13].

$$\Delta G_A = - 2.303 RT \text{ Log } K_A \quad (3)$$

$$\Delta G_A = \Delta H_A - T \Delta S_A$$

From the densities measurements of solvents (MeOH-DMF) and the densities of $\text{Cu}(\text{NO}_3)_2$ 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 Goma [14], i.e, the relation between Vander Waals volume (VW) 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 (ϕ_v) were also calculated by the following eq. (6)[15].

$$\phi_v = \frac{M_2}{d_o} - 1000 (d - d_o) / (m_s d_o) \quad (6)$$

Where, (M_2) is the M.Wt of DMF, (d_o) is the density of the solvent and (m_s) is the molality .

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

$$V = N \pi \sigma^3 / 6 \quad (7)$$

$$r_s = \sigma / 2$$

Table 1. The molar volume (V), solvated Vander Waals(V_w) and electrostriction volumes (V_e) of Cu(NO₃)₂ in (MeOH-DMF) mixtures at different temperatures

Vol% MeOH	V(cm ³ .mol. ⁻¹)				V _w (cm ³ .mol. ⁻¹)				V _e (cm ³ .mol. ⁻¹)			
	298.15K	303.15K	313.15K	313.15K	298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K
0	77.20	77.81	77.90	78.52	51.02	51.43	51.49	51.90	-26.18	-26.38	-26.41	-26.62
20	65.42	65.91	65.99	66.33	43.24	43.56	43.61	43.84	-22.18	-22.35	-22.38	-22.49
40	55.45	55.88	56.07	56.40	36.65	36.93	37.06	37.28	-18.8	-18.95	-19.01	-19.12
100	40.76	41.16	41.26	41.47	26.94	27.20	27.27	27.41	-13.02	-13.96	-13.99	-14.06

Table 2. The apparent molar volumes (φ_v), the solvated radius(r_s) and the apparent molar volume at infinite dilution (φ_v^0) of Cu(NO₃)₂ in (MeOH – DMF) mixtures at different temperatures

Vol% MeOH	$\varphi_v \times 10^3$				$r_s \times 10^{-8}$				φ_v^0
	298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K	
0	-7.84	18.67	-30.63	26.87	3.12	3.14	3.14	3.15	16
20	21.86	46.62	2.83	2.84	2.96	2.96	2.97	2.97	32
40	-193.78	-155.17	-167.18	-169.64	2.80	2.80	2.81	2.82	-40
100	30.24	68.76	38.614	9.795	2.52	2.54	2.54	2.54	-3

Table 3. The values of C, Λ , Λ_o , S(z), γ_{\pm} , α , K_A and ΔG of Cu(NO₃)₂ in mixed (MeOH-DMF) solvents at different temperatures using Fuoss – Shedlovesky method**a) at 298.15K**

Vol% of MeOH	C _m x10 ⁻⁵	Λ	Λ_o	γ_{\pm}	α	S(z)	K _A x10 ⁶	- ΔG
0	8.0	154.4	175	0.9438	0.882	1.0	7.52	39.25
20	8.0	116.3	132.5	0.9396	0.877	1.0	7.99	39.40
40	8.0	149.4	170	0.9361	0.878	1.0	7.95	39.39
100	8.0	158.8	180	0.9284	0.882	1.0	7.77	39.34

b) at 303.15K

Vol% of MeOH	C _m x10 ⁻⁵	Λ	Λ_o	γ_{\pm}	α	S(z)	K _A x10 ⁶	- ΔG
0	8.0	108	122	0.9428	0.885	1.0	7.26	39.82
20	8.0	103.9	118	0.9386	0.881	1.0	7.76	39.99
40	8.0	151	172	0.9351	0.878	1.0	8.06	40.08
100	8.0	155.5	176	0.9271	0.884	1.0	7.67	39.96

c) at 308.15K

Vol% of MeOH	C _m x10 ⁻⁵	Λ	Λ_o	γ_{\pm}	α	S(z)	K _A x10 ⁶	- ΔG
0	8.0	230	265	0.9417	0.867	1.0	8.89	40.99
20	8.0	130.6	155	0.9379	0.842	1.0	11.68	41.69
40	8.0	162.5	190	0.9337	0.855	1.0	10.36	41.39
100	8.0	169.6	197.5	0.9254	0.858	1.0	10.17	41.34

d) at 313.15K

Vol% of MeOH	C _m x10 ⁻⁵	Λ	Λ_o	γ_{\pm}	α	S(z)	K _A x10 ⁶	- ΔG
0	8.0	332	275	0.9402	0.844	1.0	11.50	42.33
20	8.0	130	160	0.9365	0.813	1.0	15.57	43.12
40	8.0	168.5	205	0.9322	0.822	1.0	14.41	42.92
100	8.0	174	210	0.9234	0.828	1.0	13.80	42.81

C in (mol./l.); Λ & Λ_o in (Ω -l. cm². mol⁻¹); K_A in (mol./l.); ΔG in (Kj. mol⁻¹)**Table 4.** The Values of C, Λ , Λ_o , γ_{\pm} , S(z), α , K_A and ΔG of Cu(NO₃)₂ in presence of Kryptofix-221 and in (MeOH-DMF) mixtures, at different temperatures using Fuoss-Sheslovesky method**a) at 298.15K**

Vol% of MeOH	C _m x10 ⁻⁵	Λ	Λ_o	γ_{\pm}	S(z)	α	K _A x10 ⁶	- ΔG
0	8.0	658.3	760	0.9418	1.0066	0.872	9.008	39.702
20	8.0	246.7	410	0.9474	1.0085	0.606	78.89	39.89
40	8.0	33	46.7	0.9373	1.0092	0.713	36.63	39.86
100	8.0	546.7	640	0.9258	1.0083	0.861	10.57	40.09

b) at 303.15K

Vol% of MeOH	C _m x10 ⁻⁵	Λ	Λ_o	γ_{\pm}	S(z)	α	K _A x10 ⁶	- ΔG
0	8.0	875	780	0.9436	1.0	0.865	9.11	40.39
20	8.0	308.5	370	0.9403	1.0	0.833	12.66	43.87
40	8.0	297.5	345	0.9358	1.0	0.862	9.57	42.76
100	8.0	467.5	740	0.9382	1.0	0.631	64.66	45.34

c) at 308.15K

Vol% of MeOH	C _m x10 ⁻⁵	Λ	Λ _o	γ ±	S(z)	α	K _A × 10 ⁶	-Δ G
0	8.0	665	790	0.8426	1.0	0.841	11.66	41.69
20	8.0	290	380	0.9409	1.0	0.763	23.512	44.21
40	8.0	275	370	0.9381	1.0	0.743	27.75	43.34
100	8.0	452.5	680	0.9342	1.0	0.665	50.82	45.46

d) at 313.15K

Vol% of MeOH	C _m x10 ⁻⁵	Λ	Λ _o	γ ±	S(z)	α	K _A × 10 ⁶	-Δ G
0	8.0	655	780	0.9404	1.0	0.839	11.95	42.43
20	8.0	288	364	0.9374	1.0	0.791	18.73	42.69
40	8.0	280	346	0.9328	1.0	0.809	16.15	42.61
100	8.0	462	380	0.9250	1.0	0.822	14.56	42.94

C in (mol/L); Λ & Λ_o in (Ω⁻¹.cm².mol⁻¹); K in (mol/L); Δ G in (Kj. Mol⁻¹)

Where (V) is the molar volume, (N) is Avogadro's number and (σ) is the diameter, the evaluated data are given in Table(2).

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.

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_o} + \frac{K_A}{\Lambda_o^2} [C \Lambda \gamma^2 S(z)] \quad (8)$$

Where S(z) = 1 + Z + Z²/2 + Z³/3 + etc

$$(Z) = \frac{S(C)^{1/2}}{\Lambda_o^{3/2}} \Lambda \quad (9)$$

Where S = a Λ_o + b, a = 8.2 × 10⁵ / (Λε T)^{3/2}, b = $\frac{0.825}{\eta_o(\epsilon T)^{1/2}}$
and

$$\text{Log } \gamma \pm = -A(\alpha C)^{1/2} [1 + Br^o(\alpha C)^{1/2}] \quad (10)$$

$$\alpha = \Lambda S(z) / \Lambda_o \quad (11)$$

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

Table (5) (a,b,c), illustrated the thermodynamic parameters (η_oΔ G_s), (Δ H_s) and (T Δ 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 (Δ G_s) values found to be increased by increasing the content of the organic solvent (MeOH-DMF) mixtures.

On the other hand, the values of (Δ H_s) and (T Δ S)_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 ($\frac{1}{T}$) at different temperatures, give slope and from their slopes, we can calculate the thermodynamic parameters (Δ H_A).

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

The graphical presentation of the relation between the association free energies (Δ 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 (φ_v) and (\sqrt{ms}), where (\sqrt{ms}) 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. K_A values increased by increase methanol content in the mixed solvents due to the preferential solvation 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 ΔG , ΔH and $T\Delta S$ of Cu(NO₃)₂ in mixed (MeOH-DMF) solvents in presence and absence of Kryptofix-221 at different temperatures

a)

Vol% MeOH	$\Delta G_A \times 10^3$ (J.mol ⁻¹)				$(\Delta G_S) \times 10^3$ (J.mol ⁻¹)				$(\Delta H)_A \times 10^3$ (J.mol ⁻¹)	$(\Delta H)_S \times 10^3$ (J.mol ⁻¹)
	298.15k	303.15k	308.15k	313.15k	298.15k	303.15k	308.15k	313.15k		
0	-39.7	-40.39	-41.69	-42.43	-39.25	-39.82	-40.99	-42.33	-14.36	-22.73
20	-39.89	-43.87	-44.21	-42.69	-39.40	-39.99	-41.69	-43.12	-15.79	-34.7
40	-39.86	-42.76	-43.34	-42.61	-39.39	-40.08	-41.39	-42.92	-14.36	-29.91
100	-40.09	-45.34	-45.46	-42.94	-39.34	-39.96	-41.34	-42.81	-16.75	-29.91

b)

Vol% MeOH	$(T\Delta S)_A \times 10^3$ (J.mol ⁻¹)				$(T\Delta S)_S \times 10^3$ (J.mol ⁻¹)			
	298.15k	303.15k	308.15k	313.15k	298.15k	303.15k	308.15k	313.15k
0	16.52	17.09	18.26	19.06	25.34	26.03	27.33	28.07
20	4.7	5.29	6.99	8.42	24.1	28.08	28.42	26.9
40	9.48	10.17	11.48	13.01	25.5	28.4	28.98	28.25
100	9.43	10.05	11.43	12.09	23.34	28.59	28.71	26.19

c) The values of $(\Delta G)_c$ of the complexation of Cu(NO₃)₂ with kryptofix-221 in mixed (MeOH-DMF) solvents at different temperatures.

Vol% MeOH	$(\Delta G)_c \times 10^3$ (J.mol ⁻¹)			
	298.15k	303.15k	308.15k	313.15k
0	-0.452	-0.57	-0.7	-0.1
20	-0.49	-3.88	-2.52	-0.43
40	-0.47	-2.68	-1.95	-0.31
100	-0.75	-5.38	-4.12	-0.13

Table 6. The values Log K_A of Cu(NO₃)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	313.15K	313.15K	298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K
0	6.95	6.96	7.06	7.07	3.46	3.37	3.46	3.47	3.170	3.051	3.11	3.19
20	6.98	7.55	7.49	7.12	3.73	3.49	2.73	3.64	2.88	2.89	2.78	3.20
40	6.98	7.36	7.35	7.11	3.79	3.38	3.79	3.58	2.82	3.36	2.60	2.76
100	7.02	7.8	7.7	7.16	4.01	4.09	4.01	3.63	4.29	4.40	4.23	3.81

K_A in (mol/L)

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