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Conductometric Studies of Ionic Association of Divalent Asymmetric Electrolyte $Cu(NO_3)_2$ with Kryptofix -22 in Mixed (MeOH-DMF) Solvents at Different Temperatures

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Abstract On using conductometric technique, new equation is applied for calculation of apparent association constant (K_A). The association constant (K_A) were studied and calculated for $Cu(NO_3)_2$ in absence and presence of Kryptofix-22 [1,7,10,16 tetra oxa 4,13 diaze cyclo octa decane] in mixed [MeOH-DMF] solvents at different temperatures. From the experimental results, the molar conductivities (Λ) is evaluated. The limiting molar conduclivities (Λ_o) were also calculated by using Shedlovsky and Fouss-Kraus extrapolation method. The Gibbs free energies of association (ΔG_A) were estimated in absence and presence of Kryptofix-22, and from these date, we calculated $\Delta G_{(Complexing)}$. We also calculated the value of enthalpy (ΔH_A) and entropy (ΔS_A) For $Cu(NO_3)_2$ in absence and presence of Kryptofix-22. In addition to (K_A), (ΔG_A), (ΔH_A), and all the previous results, the molar volume (V), solvated radius (r_s), Van der Waals (V_w), electrostriction Volume (V_e) and apparent molar volume (ϕ_V)were also calculated. All the results were discussed.

Keywords Conductometry, Kryptofix-22, Association, $Cu(NO_3)_2$, (MeOH-DMF)solvents, Van der Waals volume, Molar solvated volume, Electrostriction volume, Apparent molar volume, Limiting conductance, Free energy of association

1. Introduction

Although alkali and alkaline earth metal cations plays an important role both in chemistry and in biology, the coordination chemistry of alkali and alkaline earth metals was completely ignored by chemists. However, the coordination chemistry for alkali and alkaline earth cations has mainly developed by the synthesis of crowns by Pedersen[1]. The discovery of the crown ethers soon followed by synthesis of macrobicyclic polyether containing three polyether strands joined by two bridgehead nitrogen's[2]. These compounds have three-dimensional cavities which can accommodate metal ion of suitable size and form an inclusion complex. These ligands which developed by Lehn and his-coworkers [3] were called 2- crptands where (2) indicated the bicyclic ligand such as Kryptofix-22 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 solutions with univalent and bivalent metals[4]. The characteristic chemistry of crown ethers involves complexation of the ether oxygen's with various ionic species. This is termed "host-guest" chemistry, while the crown ether acts as host and the ionic species as guest. Crown ethers may be used as phase- transfer catalysts and as agents to promote solubility of inorganic salts in organic solution.

For example, "purple benzene" is solution of benzene, 18-crown -6, and potassium permanganate that finds utility as an oxidizing agent. The crown ether dissolved in benzene, the permanganate is forced to dissolve in benzene in order to form ion-pair with the potassium ion. This type of chemistry (host-guest) is found in nature with cyclodextrins and macrocyclic polyether antibiotics[5]. Crown ethers are not the only macrocyclic ligands that have affinity for the potassium cation. Lonophores such as nonactin and balinomycin also display marked preference for the potassium cation over other cations. "Aza-crowns" consists of crown ethers where in an ether oxygen has been replaced by an amine group. A well –known tetraza crwon is cyclen. Mixed amine- ether crowns are also known[6]. It is important to mention that the multidentate macromolecules (MMM) which have been studied as ligands for M^{+z}, were included natural antibiotics and synthetic compounds such as crowns and cryptands[7]. The antibiotics compounds could be cyclic or acyclic, where as the synthetic ligands could be acyclic, monocyclic or polycyclic. The macro molecular ligands had recently become important more than the conventional ligands to the chemistry of M^{+z}, this was primarily because they binded M^{+z} effectively and rendered the latter soluble in non-polar

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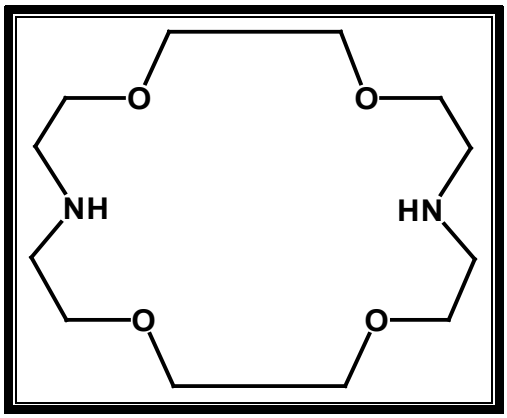
solvents and secondly because they were more relevant to the chemistry of M^{+z} in biological systems which therein involved essentially the macrobiomolecules. The strong (M^{+z}-MMM) interaction was due to the multichelate effect. The macrocyclic crown ethers have many applications[8] in biological activity, corrosion chemistry, analytical chemistry, phase-transfer catalysis and industrial production such as nuclear energy, electronics and electrochemical photosensitive materials[9]. Crown ethers find many important applications and uses. These include preparative organic chemistry, solvent extraction, phase transfer catalysis, stabilization of uncommon or reactive oxidation states and the promotion of other improbable reaction such as; the solubility of alkali metal salts in organic media can be promoted using crowns due to presence of large hydrophobic organic ring in the ligand e.g. KOH and $KMnO_4$ can be used as an alkali and an oxidizing agent, respectively in organic media also, mixed metal complexes of the alkalis can be prepared by exploitation of selectivity and differential stabilities of alkaloids and metal complex, for example K-Na alloy reacts with the crown 18-C-6 to give $[K(18\text{-}C\text{-}6)]^{+}$ Na^{-} as the product which contains both the alkali metals, one as cation and other anion. Crown ethers can sometimes act as second coordination[10]. Sphere ligands e.g. $[Pt(bipy)(NH_3)_2]^{+2}$ gives crystalline compound $[Pt(bipy)(NH_3)_2(18\text{-}C\text{-}6)]^{+2}$ with (18-C-6). Also crown ethers have applications and uses in biochemistry branch, since these ligands can imitate some biologically occurring natural compounds they are expected to provide insight into the biological phenomena occurring in living system, for example the mechanism of the sodium pump occurring across a cell membrane could be understood using the formation of the alkali metal-crown complex mechanism as a model. On understanding the interaction between macrocyclic crown ether such as Kryptofix-22 and metal cations in solutions, it requires the study of various parameters governing these interaction. The thermodynamic studies of these interactions resulted important in formation about their complication reactions and the selectivities of these ligands towards different metal cations[11]. The conductometric measurement is one of the solutions of low dielectric constants. The observed 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 dimension to the problem[12]. A conductance study of the interaction between Co^{+2}, Ni^{+2}, Ni^{+2}, $Cu^{+2}Cd^{+2}$, $Zn^{+2}$and pb^{+2} ions with cryptand-221, c-211 , c-222 in different (MeOH-DMF) mixtures was carried out at various temperatures by shamsipur[13]. The formation constants were determined from the molar conductance–mole data. The enthalpy and entropy data of the cryptate formation reaction were determined from the temperature dependence of the formation constants.

Cupper represent the back bone of these work, due to Cu take part in many chemical and biochemical events. As, biochemically, when Cupper accumulate in the body, it cause Wilson's disease (hepato lenticular degeneration) as these disease leads to finally to hemolysis and necrosis (destruction of liver cell). In our branch of chemistry Cupper as $Cu(NO_3)_2$ may be found in our experimental work and cause interference and wrong results. The aim of the present work is to study the separation of $Cu(NO_3)_2$ and study of conductivity of $Cu(NO_3)_2$ in the absence and in the presence of Kryptofix-22 by using different molar ratios of [MeOH-DMF] mixed solvents at different temperatures. By applying Shedlovsky, Fouss- Kraus extrapolations and Fuoss- Edlson methods, we were able to evaluate the values of (Λ_o), (K_A), (ΔG_A), (ΔH_A) and (ΔS_A) and to make an acceptable discussion.



[1,7,10,16 tetra oxa 4,13 diaza cyclo octa decane]
M.P = 111-114℃ Safety:- irritant M.wt=262.5 gm/mol

Figure 1. Kryptofix- 22

2. Exprimental

The aza-crown (Kryptofix-22), [1,7,10,16 tetra 4,13 diaza cyclo octa decane] was supplied from Merck co.

Where as, 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 $Cu(NO_3)_2$ was determined by using (Mettler DL-18) Karl-Fisher titrator and it was found to be less than $\pm 0.01\%$. The solvents used are MeOH (methanol) and DMF (dimethyl formamide) were BDH supplements. All the conductometric titrations were manupliated and were conducted using 1×10^{-3} mole/L $Cu(NO_3)_2$ and 1×10^{-4} mole/L Kryptofix-22 as initial concentrations. These conductometric measurements achieved by Beck mean conductivity Bridge model No. (RE-18A) in presence of Kryptofix-22. Spectrophotometrical contineous variation study of $Cu(NO_3)_2$ in the presence of Kryptofix-22 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).

The conductometer was an ultra – thermostatic connected with water- bath of the type Kotterman – 4130.

3. Results and Discussion

The specific conductance values (K_s) of different con-

centrations of $Cu(NO_3)_2$ in [MeOH-DMF] solvents in the absence and in the presence of Kryptofix-22, were measured experimentally and from which the values of molar conductance (Λ) where calculate[14] by using eq (1).

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

Where (K_s) and (K_{solv}) are the specific conductances of the solutions and the solvent, respectively; (K_{cell}) is the cell constant and (C) is the molar concentration of $Cu(NO_3)_2$.

From the density measurements of pure solvents, of mixed organic solvents (MeOH-DMF), the molar volume (V) where calculated. The packing density (P) as reported by Kim[15], i.e, the relation between Vander Waals volume (V_W) and the molar volume (V) of relatively large molecules was found to be constant value equal to 0.661.

$$\mathrm{P} = \frac{Vw}{V} = 0.661 \quad (2)$$

Where, V = M / d

The electrostriction volume (Ve), which is the volume compressed by the solvent can be calculated by using

$$Ve = (V_W - V) \quad (3)$$

The experimental date of (Λ) and (Λ_o) were analyzed firstly by using Shedlovesky extrapolation method[16] to estimate (K_A) of $Cu(NO_3)_2$ in the presence of Kryptofix-22 through sequence of the equations as follow:

$$\frac{1}{\Lambda(S(Z))} = \frac{1}{\Lambda_O} + \left(\frac{KA}{\Lambda_O^2}\right)(C\Lambda\gamma^2 \quad S(Z) \quad (4)$$

Where S (Z)= 1+Z+Z $^2/_2$ +Z $^3/_8$ + …… etc

Due to

$$S(Z) = \left[\frac{Z}{2} + \left(1 + \left(\frac{Z}{2}\right)^2\right)^{\frac{1}{2}}\right]^2 \quad (5)$$

$$\therefore (Z) = \frac{S(\Lambda C)^{\frac{1}{2}}}{\Lambda o^{\frac{3}{2}}} \quad (6)$$

$$S = a\Lambda o + b \quad (7)$$

$$a = \frac{8.2 \times 10^5}{(\varepsilon T)^{\frac{3}{2}}} b = \frac{0.825}{\eta_o (\varepsilon T)^{\frac{1}{2}}} \quad (8)$$

$$\log \gamma \pm = -A(\alpha C)^{\frac{1}{2}}\left[1 + Br^{\circ}(\alpha C)^{\frac{1}{2}}\right] \quad (9)$$

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 solvents, respectively.

The association constants (K_A) for different concentrations of $Cu(NO_3)_2$ in mixed (MeOH-DMF) solvents in absence and presence of Kryptofix-22 were calculated by applying new equation (equation13) derived as:

$$A^{+2} + 2B^{-} \rightleftharpoons AB_2 \quad (10)$$

$$K_A = \frac{1-\alpha}{4cm^2\gamma \pm^2 \alpha^3} \quad (11)$$

Where,

$$\alpha = \frac{\Lambda(S(Z))}{\Lambda o} \quad (12)$$

Substitute (α) by equation (12) in equation (11) we obtain:

$$K_A = \frac{\Lambda_o^2(\Lambda_o - \Lambda)}{4Cm^2\gamma \pm^2 \Lambda^3 S(Z)} \quad (13)$$

All the parameters calculated by Shedlovesky method are given in Tables 1,2 (at four different temperatures in presence and absence of Kryptofix-22), these parameters such as:- (C_m, Λ, Λ_o, $\gamma \pm$, S(Z), α, K_A).

The evaluation of Gibbs free energies of association give as follow:

$$\Delta GA = -RT \ln KA \quad (14)$$

And also we calculated ΔG_A without Kryptofix-22 and we calculated $\Delta G_{(complexing)}$ as show in Table (5) and we calculated ΔH_A from the slope of plot of (log k_A and $^1/_T$), we can calculate ΔH from slope

Where slope = - ΔH_A /2.303R

And calculating (ΔS_A) from Gibbs equation as show in table 3,4

$$\Delta G_A = \Delta H_A - T\Delta S_A \quad (15)$$

From the data of densities and molality , apparent molar volume (ϕ_v) were calculated as follow:

$$\varphi_v = \frac{M_2}{d_o} - 1000(d - do/(m_s ddo) \quad (16)$$

Also solvated radii of $Cu(NO_3)_2$ were calculated by using equation (16) as follow[17].

$$V = NA\Pi\sigma^3 / 6 \quad (17)$$

Where:- V: molar volume

N_A: Avogadro's number = 6.023×10^{23}

Then

$$r_s = \frac{\sigma}{2} \quad (18)$$

Where (r_s) is the solvated radius.

All these parameters such as (V, V_w, V_e, ϕ_V and r_s) of $Cu(NO_3)_2$ in (MeOH-DMF) solvents at different temperatures were calculated and given in Table (6) following equation 16.

when we make relation between ϕ_V and $\sqrt{ms}$ as :-

$$\varphi_v = \varphi_v^o + S_v\sqrt{ms} \quad (19)$$

Where, $ms = \frac{8 \times 10^{-5}}{d}$

The slope equal to (S_v), and the intercept equal to $(\phi^{\circ}v)$.

It was concluded from Table (7) that the association constants (K_A) of $Cu(NO_3)_2$ in the presence of Kryptofix-22 in (MeOH-DMF) mixture, using the methods (Fuoss and Fuoss-Kraus) have nearly same value. This indicated that the association constants in this case are due to the formation of different stiochiometric complexes. The formation of these complexes are probably be outside the Kryptofix ring.

Table 1. The values of concentration (Cm), molar conductance ($_{\circ}\Lambda$), limiting molar conductance ($\gamma \pm$), activity coefficient (Λ), Fouss-Shedlovsky parameter S(Z) and association constant(KA) of $Cu(NO_3)_2$ with Kryptofix-22 in [MeOH-DMF] solvents at different temperatures

A- at 298.15 K

Vol% of MeOH	C_m	Λ	$_{o}\Lambda$	$\gamma \pm$	S(Z)	α	K_A
0	8×10^{-5}	647.1	810	0.9465	1.010	0.807	17.1×10^{6}
20	8×10^{-5}	346.5	396	0.9398	1.0126	0.886	8.14×10^{6}
40	8×10^{-5}	90	250	0.9587	1.0119	0.364	57.6×10^{6}
100	8×10^{-5}	526.3	670	0.9324	1.0141	0797	19.6×10^{6}

B- at 303.15 K

Vol% of MeOH	C_m	Λ	$_{o}\Lambda$	$\gamma \pm$	S(Z)	α	K_A
0	8×10^{-5}	670	760	0.9431	1.0	0.882	7.61×10^{6}
20	8×10^{-5}	340	340	0.9390	1.0	0.872	8.57×10^{6}
40	8×10^{-5}	100	162.2	0.9454	1.0	0.615	7.21×10^{6}
100	8×10^{-5}	530	635	0.9293	1.0	0.835	12.9×10^{6}

C- at 308.15 K

Vol% of MeOH	C_m	Λ	$_{o}\Lambda$	$\gamma \pm$	S(Z)	α	K_A
0	8×10^{-5}	663.3	760	0.9416	1.0	0.873	8.41×10^{6}
20	8×10^{-5}	335	400	0.9382	1.0	0.837	12.27×10^{6}
40	8×10^{-5}	90	210	0.9527	1.0	0.429	31.24×10^{6}
100	8×10^{-5}	525	630	0.9267	1.0	0.833	13.10×10^{6}

D- at 313.15 K

Vol% of MeOH	C_m	Λ	$_{o}\Lambda$	$\gamma \pm$	S(Z)	α	K_A
0	8×10^{-5}	660	810	0.8206	1.0	0.815	19.8×10^{6}
20	8×10^{-5}	330	420	0.7927	1.0	0.786	27.51×10^{6}
40	8×10^{-5}	65	310	0.2108	1.0	0.209	7.54×10^{10}
100	8×10^{-5}	470	780	0.6075	1.0	0.603	19.22×10^{7}

Table 2. The values of concentration (C_m), molar conductance (Λ), limiting molar conductance ($_{\circ}\Lambda$), activity coefficient ($\gamma \pm$), Fouss-Shedlovsky parameter S(Z) and association constant(K_A) of $Cu(NO_3)_2$ without Kryptofix-22 in [MeOH-DMF] solvents

A- at 298.15 K

Vol% of MeOH	C_m	Λ	$_{o}\Lambda$	$\gamma \pm$	S(Z)	α	K_A
0	8×10^{-5}	154.4	175	0.9438	1.0	0.882	7.51×10^{6}
20	8×10^{-5}	116.3	132.5	0.9396	1.0	0.877	7.91×10^{6}
40	8×10^{-5}	149.4	170	0.9361	1.0	0.879	7.96×10^{6}
100	8×10^{-5}	158.8	180	0.9284	1.0	0.882	7.77×10^{6}

B- at 303.15 K

Vol% of MeOH	C_m	Λ	$_{o}\Lambda$	$\gamma \pm$	S(Z)	α	K_A
0	8×10^{-5}	108	122	0.9428	1.0	0.885	7.26×10^{6}
20	8×10^{-5}	103.9	118	0.9386	1.0	0.880	7.76×10^{6}
40	8×10^{-5}	151	172	0.9351	1.0	0.878	8.06×10^{6}
100	8×10^{-5}	155.5	176	0.9271	1.0	0.883	7.67×10^{6}

C- at 308.15 K

Vol% of MeOH	C_m	Λ	$_{o}\Lambda$	$\gamma \pm$	S(Z)	α	K_A
0	8×10^{-5}	230	265	0.9417	1.0	0.868	8.89×10^{6}
20	8×10^{-5}	130.6	155	0.9379	1.0	0.842	11.68×10^{6}
40	8×10^{-5}	162.5	190	0.9337	1.0	0.855	10.36×10^{6}
100	8×10^{-5}	169.6	197.5	0.9254	1.0	0.859	10.17×10^{6}

D- at 313.15 K

Vol% of MeOH	C_m	Λ	$_{o}\Lambda$	$\gamma \pm$	S(Z)	α	K_A
0	8×10^{-5}	232	275	0.9402	1.0	0.844	11.50×10^{6}
20	8×10^{-5}	130	160	0.9365	1.0	0.812	15.56×10^{6}
40	8×10^{-5}	168.5	205	0.9322	1.0	0.822	14.41×10^{6}
100	8×10^{-5}	174	210	0.9234	1.0	0.829	13.80×10^{6}

Λ C in (mol/L) ; $_{o}$ in (Λ^{-1}. Cm^2. mol^{-1}) ; K_A in (mol/L) Ω

Table 3. The enthalpies (ΔHA) and entropies (ΔSA) of $Cu(NO_3)_2$ with Kryptofix -22 at different temperatures

Vol% of MeOH	(ΔS_A)				(ΔH_A)
temp	298.15	303.15	308.15	313.15	
0	114.04	107.87	109.04	116.55	-0.72×10^4
20	117.39	113.14	113.91	129.33	-0.64×10^4
40	106.32	101.60	102.54	137.9	-0.96×10^4
100	128.79	125.35	125.6	148.02	-0.32×10^4

Table 4. The enthalpies (ΔHA) and entropies (ΔSA) of $Cu(NO_3)_2$ without Kryptofix -22 at different temperatures

Vol% of MeOH	(ΔS_A)				(ΔH_A)
temp	298.15	303.15	308.15	313.15	
0	57.35	58.38	61.01	64.50	-2.21×10^4
20	34.21	35.62	40.56	44.71	-2.91×10^4
40	68.08	68.94	72.04	76.11	-1.91×10^4
100	29.18	30.68	34.72	38.83	-4.14×10^4

Table 5. The Gibbs free energies (ΔGA) of $Cu(NO_3)_2$ in presence and absence of Kryptofix-22 and (ΔGcomplexing) at different temperatures

Vol% of MeOH	($\Delta G_A \times 10^4$) In presence of Kryptofix-22				($\Delta G_A \times 10^4$) In absence of Kryptofix-22				$\Delta G_{complexing}$			
temp	298.15	303.15	308.15	313.15	298.15	303.15	308.15	313.15	298.15	303.15	308.15	313.15
0	-4.12	-3.99	-4.08	-4.37	-3.92	-3.98	-4.09	-4.23	-2000	-100	100	-1400
20	-4.14	-4.07	-4.15	-4.69	-3.93	-3.99	-4.16	-4.31	-2100	-800	100	-3800
40	-4.13	-4.04	-4.12	-5.28	-3.94	-4	-4.13	-4.29	-1900	-400	100	100
100	-4.16	-4.12	-4.19	-4.9	-3.93	-3.99	-4.13	-4.28	-2300	-1300	-200	-6800

Table 6. The values of molar volume (V), Van der Waals (Vw) and electrostriction volume (Ve) of $Cu(NO_3)_2$ in (MeOH-DMF) solvents at different temperatures

Vol% of MeOH	molar volume (V)				Vander Waals (Vw)				electrostriction volume (Ve)			
temp	298.15	303.15	308.15	313.15	298.15	303.15	308.15	313.15	298.15	303.15	308.15	313.15
0	77.21	77.82	77.91	78.53	51.04	51.44	51.5	51.91	-26.17	-26.38	-26.41	-26.62
20	65.42	65.82	65.90	66.24	43.18	43.51	43.56	43.78	-22.15	-22.31	-22.34	-22.5
40	55.42	55.85	56.04	56.37	36.63	36.9	37.04	37.26	-18.79	-18.95	-19	-19.11
100	40.77	41.16	41.27	41.48	26.95	27.21	27.28	27.42	-13.82	-13.95	-13.99	-14.06

Table 7. The values of solvated radii (rs) , apparent molar volume (ϕv) and $(\varphi^{\circ}v)$ of $Cu(NO_3)_2$ in (MeOH-DMF) solvents at different temperatures

Vol% of MeOH	[solvated radii (rs) ×103]				[apparent molar volume (ϕ v) ×10-8]				(ϕ0 v)
temp	298.15	303.15	308.15	313.15	298.15	303.15	308.15	313.15	
0	-7.849	18.8	-30.6	26.9	3.12	3.14	3.14	3.15	20
20	21.9	46.6	2.83	2.85	2.96	2.96	2.97	2.97	32
40	-193.8	-155.2	-167.2	-169.6	2.80	2.80	2.81	2.82	-40
100	30.2	68.7	38.5	9.79	2.52	2.54	2.54	2.54	-3

Table 8. Log KA values according to this work , Fuoss-Shedlovsky and Fuoss-Kraus for the interaction of $Cu(NO_3)_2$ with Kryptofix-22 at different temperatures

Vol% of MeOH	log K_A				log K_A (Fuoss)				log K_A- F_k			
temp	298.15	303.15	308.15	313.15	298.15	303.15	308.15	313.15	298.15	303.15	308.15	313.15
0	7.233	6.881	6.926	7.297	3.621	3.296	3.338	3.567	3.170	3.203	3.59	3.17
20	7.268	7.027	7.046	7.827	3.326	3.340	3.484	3.665	3.27	3.47	3.42	3.47
40	7.239	6.968	6.989	8.807	4.814	4.130	4.616	4.372	4.25	6.55	4.71	4.19
100	7.292	7.109	7.117	8.283	3.671	3.502	3.508	4.117	3.69	3.66	3.30	5.09

4. Conclusions

It was concluded that the (K_A) associations of Cupper ions with kryptofix-22 increases with increase of temperature and the content of methanol in the mixed solvents due to the increase of ion-solvent interactions.

(K_A) values obtained here be applying the new equation give suitable to the great number of ions and charges expected in case of Cupper salts in comparison to small values obtained by other theories.

The increase in all the thermodynamic parameters ΔG , ΔH and ΔS for complexation by increase in both methanol contents and temperatures indicate the more interaction , spontaneous and exothermic behaviours which confirm (K_A) previous values . Slight decrease of the association degrees (α) with increase of methanol contents were compensated by

the increase in complexation parameters in Fig(7)

Apparent molar volumes (ϕ_V) and ($\phi^{\circ}v$) are decreased by increasing the mole fraction of methanol in the mixed solvents because Cupper ions are more likely to interact with Kryptofix than solvation with the mixed solvents.

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