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**Md. Delwar Hossen**

Department of Chemistry,  
Faculty of Science, Mawlana  
Bhasani Science and Technology  
University, Santosh, Tangail,  
Bangladesh

**Pijush Kanti Roy**

Department of Chemistry,  
Faculty of Science, Mawlana  
Bhasani Science and Technology  
University, Santosh, Tangail,  
Bangladesh

**Md. Saddam Hossain**

Department of Chemistry,  
Faculty of Mathematical and  
Physical Sciences, Jahangirnagar  
University, Savar, Dhaka,  
Bangladesh

**Dr. DM Shafiqul Islam**

Department of Chemistry,  
Faculty of Mathematical and  
Physical Sciences, Jahangirnagar  
University, Savar, Dhaka,  
Bangladesh

## Complexation of benzo-18-crown-6 with $Zn^{2+}$ , $Co^{2+}$ and $Ni^{2+}$ ions in MeOH-water solvent mixtures by Conductometric study

**Md. Delwar Hossen, Pijush Kanti Roy, Md. Saddam Hossain and Dr. DM Shafiqul Islam**

### Abstract

The conductance behavior of some metal ions such as  $Ni^{2+}$ ,  $Co^{2+}$  and  $Zn^{2+}$  and their complexes with crown ether (Benzo-18-crown-6) have been studied in 10%, 20%, 30%, 40% and 50% MeOH-water mixed solvent at 308.15K, 313.15K, 318.15K, and 323.15K temperatures. The Conductometric studies indicate the 1:1 complex formation between the studied metal ions and crown ether, Benzo-18-crown-6. The order of stability constants with the studied crown ether is found to be  $Co(II) > Ni(II) > Zn(II)$  for all solvent compositions at all temperatures. The stability constants for all  $Ni^{2+}$ ,  $Co^{2+}$  and  $Zn^{2+}$  with crown ether complexes in MeOH-water mixed solvents were found to be increase with the increase in organic portion in the solvent composition for all temperatures. Thermodynamic parameters such as  $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$  for the complexation reactions have been determined. The stability constants of the complexes were found to be decrease with increase in temperature. The enthalpy and entropy of complexation formations were determined from the temperature dependence of the stability constants.

**Keywords:** Conductivity, stability constant, host-guest chemistry, thermodynamic parameter, molar conductance, thermodynamic stability and kinetic stability

### Introduction

Pedersen first reported this synthesis of crown ether in capable of forming selective and stable complexes with metal ions and neutral molecules. There are macrocyclic polyethers usually containing carbon, hydrogen and oxygen atoms, each oxygen atom being bonded with two carbon atoms and exhibit a conformation with a hole in between, for which the name crown is derived. The pioneering work of Pedersen (Pedersen, 1967; Pedersen, 1970) [1, 2] with crown ethers was recognized by awarding him the Nobel Prize in 1987. The knowledge of stability constant is very much important and has many applications such as in complexometric titration, calorimetric analysis, quantitative determination of the trace elements and analytical chemistry etc. The study of the formation of complexes between metal and ligand has been received considerable attention since few decades (Dawer *et al.*, 1988; Babcock and Pizer, 1987) [3, 4]. Crown ether acts as ligand (called donor atom for metal ions) are heterocycles that, in their simplest form, are cyclic oligomers of dioxane. The essential repeating unit of any simple crown ether is ethyleneoxy, i.e.  $-CH_2CH_2O-$ , which repeats twice in dioxane and six times in 18-crown-6. There is no formal definition of the transition between heterocycle and heteromacrocyclic. The nine membered ring 1, 4, 7-trioxonane (9-crown-3) is often named as a crown and can certainly interact with cations macrocycles of the  $(-CH_2CH_2O)_n$  type in which n are generally referred to as crown ethers rather than their systematic names. This is partly because they comprise a special group of heterocycles that bind cations, many examples of which have appeared in the literature (Inoue, Gokel, 1990; Gokel, 1991; Dietrich, 1993) [5-7]. Complexation by 9-crown-3 (often two molecules per cation) is known but less common. Of course, the heterocycles dioxane and tetrahydrofuran are known to serve as donors for metal ions. Typically, several molecules of THF provide multiple binding sites whereas several heteroatom donors are typically present in each crown ether. Thus, distinctions at this level may be convenient but are largely artificial. In the mid-1960s, Charles Pedersen, a chemist working at DuPont, was trying to prepare a complexing agent for divalent cations (Pedersen, 1968) [8]. His strategy was to link two catechols through one hydroxyl on each molecule. This would give him a compound that could partially envelop the cation and, by ionization of the

### Correspondence

**Md. Delwar Hossen**

Department of Chemistry,  
Faculty of Science, Mawlana  
Bhasani Science and Technology  
University, Santosh, Tangail,  
Bangladesh

phenolic hydroxyls, neutralize the bound dication. He was surprised to isolate a byproduct that bound or complexed with potassium cation but had no ionizable hydroxyl groups, Pedersen called the new material dibenzo-18-crown-6; it is shown with the intended complexing agent that was also isolated (Pedersen, 1967) [1, 9]. Pedersen realized that the polyethers represented a new class of complexing agents that were capable of binding alkali-metal cations (Pedersen, 1967) [9]. The challenging to do so with a neutral complexer was significant at that time, and such compounds were highly desirable. The main characteristic of crown ether is the complexation of the ether oxygen's with various ionic species. If metallic elements pass through the centre of the hole, they stick to oxygen's atoms. The crown compound is then termed "host-guest chemistry". Crown ether acts as the "host" taking ionic species as its "guest". Crown compound locks guest atoms in a solution and wrap around it. Crown ethers are used in PTC (phase transfer catalyst) system and in encouraging the solubility of inorganic compounds in organic solvents to promote chemical reaction. "Host-guest" chemistry of crown ethers can be a key to identify the move of essential elements in the body and can play the part of very complicated biological reactions such as enzyme's functions, which can be applied to develop new pharmaceuticals. Studies these crown ethers and their interactions with a wide variety of cation, anion and neutral molecules have become a popular field of research. Because their selectivity and extraction efficiency, crown ethers have been widely used as suitable neutral carriers for the selective transport through liquid membranes and for constructing membrane selective electrodes for different metal ions. There are various methods to study the complexation of metals with organic and inorganic ligands. The conductance measurement is a sensitive and powerful technique to study the complexation of macrocyclic crown ethers with ions in a variety of solvents.

### Experimental

The conductometric titration has been carried to obtain the equilibrium constant of complex formation. Dipe-type conducting cell made of platinum black of cell constant  $0.97 \text{ cm}^{-1}$  has been used and the cell was thermostat. The procedure was followed at four different temperature such as 308.15K, 313.15K, 318.15K and 323.15K in solvent methanol composition such as 10%, 20%, 30%, 40% and 50% (w/w) with water for benzo-18-crown-6. The temperature of the system was maintained with the help of water thermo-stated bath. In a typical run 20 mL of a metal solution ( $5 \times 10^{-3} \text{ M}$ ) was placed in a glass cell which was immersed in the water containing thermostat at a desired temperatures. The initial conductance of the solution was measured after thermal equilibrium had been reached. Then a known amount of the macrocycle solution was added in a stepwise manner using a calibrated micro-pipette. The conductance of the resulting solution was measured after each addition. Addition of the ligand was continued until the desired ligand to cation mole-ratio was achieved.

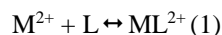
### Determination of cell constant

First the potassium chloride was recrystallized from a saturated aqueous solution and the crystals were dried to a constant weight. Then the conductivity measurements were carried out with a dip type conductivity cell made of platinum black using 0.1 and 0.01 decimal solutions of recrystallized potassium chloride. The cell constant was determined to be

$0.95 \text{ cm}^{-1}$  at  $25^\circ\text{C}$  temperature of the bath was controlled and measured with sensitivity of  $0.7^\circ\text{C}$ .

### Theory of stability constant, $K_f$

Stability constant,  $K_f$  of a complex ion is the equilibrium constant for the formation of the complex ion from the metal ion and the crown ethers. Let us consider a reaction of metal ion,  $M^{2+}$  with macro cycle, L which can be expressed by the following equation:



The corresponding equilibrium constant,  $K_f$  is given by

$$K_f = \frac{[ML^{2+}]}{[M^{2+}][L]} \times \frac{f(M^{2+})f(L)}{f(ML^{2+})} \quad (2)$$

Where,  $f$  represents the activity coefficient of the respective species. Where  $[ML^{2+}]$ ,  $[M^{2+}]$  and  $[L]$  represent the equilibrium molar concentration of complex, free cation and free ligand respectively. Under the dilute condition used the activity of uncharged ligand,  $f(L)$ , can be reasonably assume as unity. The use of the Debye-Huckel limiting law leads to the conclusion that  $f(M^{2+}) \sim f(ML^{2+})$ , so the activity coefficients equation cancel. Thus the stability constant can be expressed as,

$$K_f = \frac{[ML^{2+}]}{[M^{2+}][L]} = \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})[L]} \quad (3)$$

Where,

$$[L] = C_L - \frac{C_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_M - \Lambda_{ML})}$$

Here  $\Lambda_M$  is the molar conductance of the metal ion before addition of ligand, the molar conductance of the complexed ion, the observed molar conductance of the solution during titration, the analytical concentration of the macrocycle, added and the analytical concentration of the metallic salt.

### Determination of stability constant, $K_f$

The express of stability constant is as follows:

$$K_f = \frac{[ML^{2+}]}{[M^{2+}][L]}$$

Which can be expressed in terms of the molar conductance as

$$K_f = \frac{[ML^{2+}]}{[M^{2+}][L]} = \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})[L]} \quad (4)$$

Where,

$$[L] = C_L - \frac{C_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_M - \Lambda_{ML})} \quad (5)$$

Here  $\Lambda_M$  is the molar conductance of the metal ion before addition of ligand,  $\Lambda_{ML}$ , the molar conductance of the complexed ion,  $\Lambda_{obs}$ , the molar conductance of the solution during titration,  $C_L$ , the analytical concentration of the macro cyclic, L, added and  $C_M$  the analytical concentration of the salt.

Stability constant was determined by following through the step-wise calculation shown below:

**Step-1:** A range of molar conductance of the complex,  $\Lambda_{ML}$ ,

calculation was used in the Microsoft excel program was used from molar conductance at higher mole-ratio,  $C_L/C_M$  value that is the value when metal-ligand are supposed to be fully complexed.

Then from the equation

$$K_f = \frac{(\Lambda_M - \Lambda_{obs})(\Lambda_M - \Lambda_{ML})}{\left[ C_M \left\{ \frac{C_L}{C_M} (\Lambda_{obs} - \Lambda_{ML})(\Lambda_M - \Lambda_{ML}) - (\Lambda_{obs} - \Lambda_{ML})(\Lambda_M - \Lambda_{obs}) \right\} \right]} \quad (6)$$

Which is combined from of equation (1) and (2) we can obtain some probable values of  $K_f$  using higher mole-ratio,  $\frac{C_L}{C_M}$  and for its molar conductance ( $\Lambda_{obs}$ ) value.

**Step-2:** After evaluating the various value of  $K_f$  for various  $\Lambda_{ML}$  (which was assumed before) at higher mole-ratio, we determined the various free ligand concentration,  $[L]$ , for mole-ratio  $\frac{C_L}{C_M} \sim 1$  from the equation

$$K_f [L]^2 + (1 + K_f C_M - K_f C_L) [L] - C_L = 0 \quad (7)$$

$$\frac{K_f}{C_M} [L]^2 + \left( \frac{1}{C_M} + K_f - K_f \frac{C_L}{C_M} \right) [L] + \left( -\frac{C_L}{C_M} \right) = 0 \quad (8)$$

**Step-3:** We determined  $\Lambda_{obs}$ , using that value of various free ligand concentration,  $[L]$  at mole-ratio  $\sim 1$ , molar conductance of metal ion,  $\Lambda_M$ , concentration of metal salts,  $C_M$  and those molar conductance of complex,  $\Lambda_{ML}$

From the rearrangement of equation (5)

$$\Lambda_{obs} = \Lambda_M - \frac{C_L}{C_M} (\Lambda_M - \Lambda_{ML}) + \frac{[L]}{C_M} (\Lambda_M - \Lambda_{ML}) \quad (9)$$

**Step-4:** The observed molar conductances were compared with the calculated molar conductance. The real molar conductance is closest to the observed molar conductance. Then this is the real value of molar conductance of the complex,  $\Lambda_{ML}$ .

**Step-5:** Stability constant was then determined using that particular,  $\Lambda_{ML}$  (from step-4) mole-ratio  $\sim 1$ , observed molar conductance,  $\Lambda_{obs}$ , (at mole-ratio  $\sim 1$ )

From the equation (6)

$$K_f = \frac{(\Lambda_M - \Lambda_{obs})(\Lambda_M - \Lambda_{ML})}{\left[ C_M \left\{ \frac{C_L}{C_M} (\Lambda_{obs} - \Lambda_{ML})(\Lambda_M - \Lambda_{ML}) - (\Lambda_{obs} - \Lambda_{ML})(\Lambda_M - \Lambda_{obs}) \right\} \right]}$$

Then that was the final value of stability constant,  $K_f$ , for the complex formation of metal ligand complexation reaction.

## Result and Discussion

The changes of molar conductivity,  $\Lambda_m$  versus the ligand to the metal ion molar ratio (mole- ratio) for complexation of crown ethers with metal ions were measured in MeOH-water mixed solvents at different temperatures. This behavior indicates that the complexed metal ion is less mobile than the solvated metal ion. Figures (1-5), that in every case, addition of the crown ether (ligand) to metal ion solution causes a continuous decrease in the molar conductance. These values for stability constants of the  $Ni^{2+}$ ,  $Co^{2+}$  and  $Zn^{2+}$ - benzo-18-

crown-6 complexes in methanol-water solvents of varying composition and varying temperatures have been shown in tables (1- 3). The van't Hoff plots of  $\log K_f$  versus  $1/T$  in all cases were linear and these plots are shown in figures (6-10).

## Complex formations of metal-ligand and the ligand effect on complex formation

In order to evaluate the effect of adding crown ethers on the molar conductance of Zinc sulfate heptahydrate, Cobalt(II) sulfate and Ni (II) sulfate solution in methanol-water, the conductivity at a constant  $Zn^{2+}$ ,  $Co^{2+}$  and  $Ni^{2+}$  concentration ( $1.0 \times 10^{-4} M$ ) was considered while increasing the crown ether concentration at different temperatures. The corresponding molar conductance vs. the crown ether/metal ion mole-ratio plots are shown in figure (1-5). The changes of stability constants formed between metal ions and crown ether with the composition of MeOH in MeOH-water mixed solvents are shown in figure (11-13) at different temperatures. As is shown in figure (11-13), the changes of the stability constant ( $\log K_f$ ) of benzo-18-crown-6 complex with the metal ion versus methanol composition binary system at various temperatures are linear. This behavior is probably due to less solvent-solvent interactions between methanol and water in this studied systems.

## Solvent effects

The stability constants of the metal complexes [Nickel (II), Zinc (II) and Cobalt(II)] with crown ether benzo-18-crown-6 were determined at different temperatures in mixed aquas solutions of methanol. In general the stability constants of the metal complexes increases with increasing composition of the organic solvent in the order 50% MeOH-water > 40% MeOH-water > 30% MeOH-water > 20% MeOH-water > 10% MeOH-water. Solvent effect on stability constants were studied by using five different composition of solvent (Methanol-water) which are shown in table (1-3). Higher percentage of solvent-water mixture should be ignored. Because the metal salts cannot be dissolved in higher percentage of the solvent composition (methanol).

## The thermodynamic effect of complex formation

Table 4 show the thermodynamic parameters of the crown ether complex of  $Ni^{2+}$ ,  $Co^{2+}$  and  $Zn^{2+}$  in methanol-water solvent at various temperatures. The  $\Delta H^0$  and  $\Delta S^0$  of the complexation reactions in different solvent mixtures were calculated from the temperature dependence of the formation constants by applying a linear least-square analysis according to the van't Hoff equation. The van't Hoff plots of  $\log K_f$  versus  $1/T$  are shown in figures (1-5). The enthalpies and entropies of complexation were determined in the usual manner from the slopes and intercepts of the plots respectively and the results are listed in table 4. The standard free energy change  $\Delta G^0$  has been obtained from the well-known equations.

$$\Delta G^0 = -2.303RT \log K_f$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0$$

Where, T is the temperature of the reaction medium.

**Table 1:** Stability constant  $K_f$  for Benzo-18-crown-6- $Ni^{2+}$  complexes in aqua-organic solvent mixtures at different temperatures.

% of Organic Solvent	log $K_f$			
	308.15 K	313.15 K	318.15 K	323.15 K
10% Methanol	1.10	1.00	1.03	0.99
20% Methanol	1.21	1.10	1.15	1.17

30% Methanol	1.33	1.41	1.45	1.12
40% Methanol	1.55	1.44	1.50	1.44
50% Methanol	1.56	1.49	1.45	1.37

**Table 2:** Stability constant  $K_f$  for Benzo-18-crown-6- $\text{Co}^{2+}$  complexes in aqua-organic solvent mixtures at different temperatures.

% of Organic Solvent	log $K_f$			
	308.15 K	313.15 K	318.15 K	323.15 K
10% Methanol	1.53	1.58	1.59	1.59
20% Methanol	1.59	1.58	1.57	1.57
30% Methanol	1.48	1.49	1.48	1.43
40% Methanol	1.56	1.55	1.55	1.52
50% Methanol	1.47	1.46	1.46	1.45

**Table 3:** Stability constant  $K_f$  for Benzo-18-crown-6- $\text{Zn}^{2+}$  complexes in aqua-organic solvent mixtures at different temperatures.

% of Organic Solvent	log $K_f$			
	308.15 K	313.15 K	318.15 K	323.15 K
10% Methanol	0.82	0.83	0.81	0.77
20% Methanol	0.94	0.92	0.86	0.85
30% Methanol	1.22	1.16	1.12	1.11
40% Methanol	1.31	1.24	1.19	1.19
50% Methanol	1.53	1.48	1.46	1.45

Tables (1-3) show that the nature of solvents plays a very fundamental role in the complexation reactions. There is actually a linear relationship between the stabilities of the

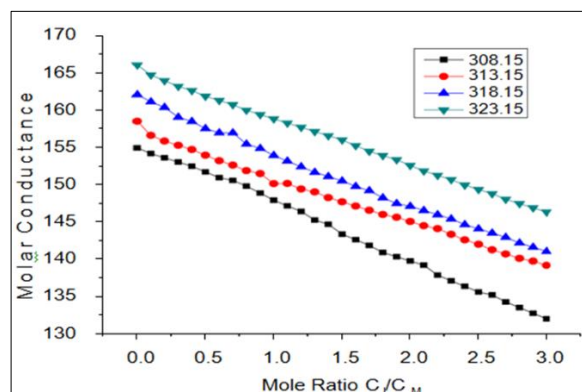
complexes as the percents of the solvent (methanol) increases the stability of the complex increases.

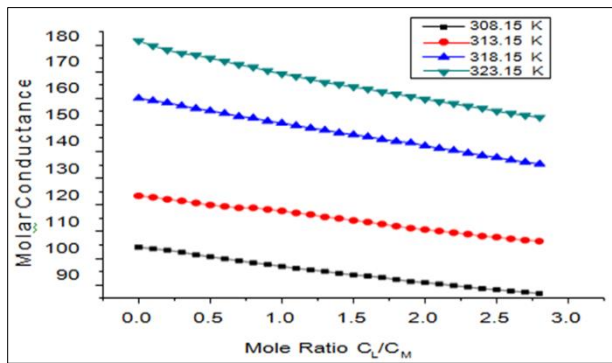
**Table 4:** Thermodynamic parameter of  $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$  for Benzo-18-Crown-6-  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  complexes in MeOH-water solvent mixture.

Complex	Composition	$-\Delta G^0$ (KJ mol <sup>-1</sup> )	$-\Delta H^0$ (KJ mol <sup>-1</sup> )	$-\Delta S^0$ (JK <sup>-1</sup> mol <sup>-1</sup> )
Benzo- 18-crown-6- $\text{Ni}^{2+}$	10%	6.50	11.80	17.67
	20%	7.13	20.13	41.13
	30%	7.84	20.37	39.11
	40%	9.12	9.74	2.49
	50%	9.03	18.63	31.01
Benzo- 18-crown-6- $\text{Co}^{2+}$	10%	8.99	1.51	25.46
	20%	9.11	2.17	23.34
	30%	8.76	6.24	8.39
	40%	9.22	4.53	15.24
	50%	8.68	3.69	16.12
Benzo- 18-crown-6- $\text{Zn}^{2+}$	10%	4.83	6.35	4.71
	20%	5.53	11.56	19.56
	30%	7.20	13.79	21.62
	40%	7.71	14.61	22.66
	50%	9.02	9.14	0.60

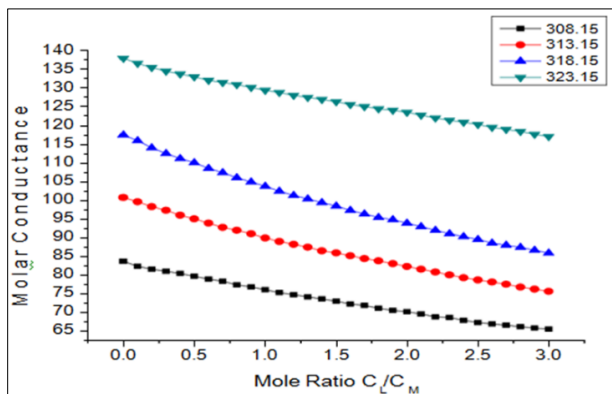
It can be seen from the data's of table 4, all thermodynamic functions of complex formation are negative. The negative  $\Delta G^0$  values indicate that the complexation reactions in these solvent mixtures are spontaneous. From table 4, it can be found that, in most cases the  $\Delta G^0$  values increase within the increase of organic portion in the solvent composition which

indicates that the complexation reactions are more spontaneous in higher organic portion of the solvent composition. The  $\Delta H^0$  values in all solvent composition were found to be negative indicating the formation of exothermic complexation reaction. The  $\Delta S^0$  values were also found to be negative.

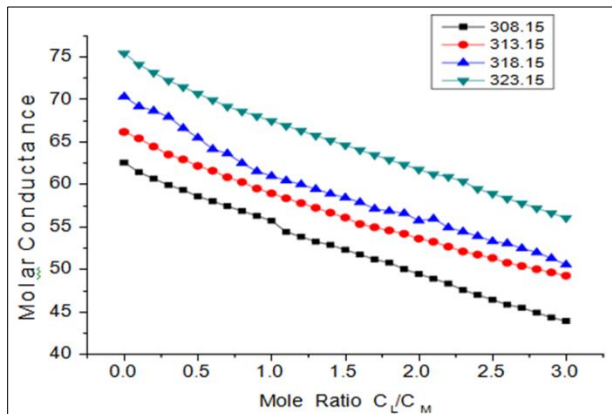
**Fig 1:** Molar conductance vs. mole-ratio plots for Benzo-18-crown-6- $\text{Ni}^{2+}$  in 10% (w/w) methanol at different temperatures.



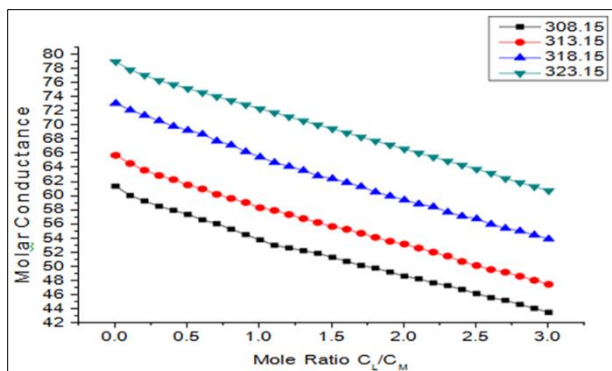
**Fig 2:** Molar conductance vs. mole-ratio plots for Benzo-18-crown-6-Ni<sup>2+</sup> in 20% (w/w) methanol at different temperatures.



**Fig 3:** Molar conductance vs. mole-ratio plots for Benzo-18-crown-6-Ni<sup>2+</sup> in 30% (w/w) methanol at different temperatures.

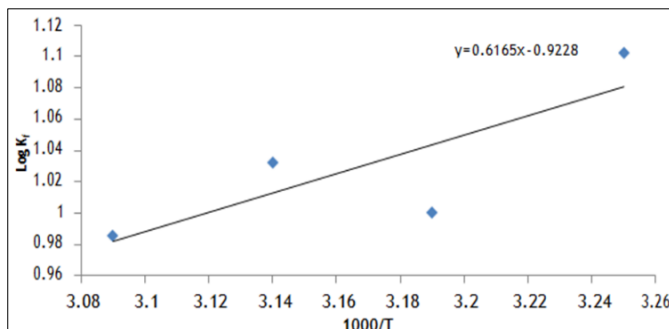


**Fig 4:** Molar conductance vs. mole-ratio plots for Benzo-18-crown-6-Ni<sup>2+</sup> in 40% (w/w) methanol at different temperatures.

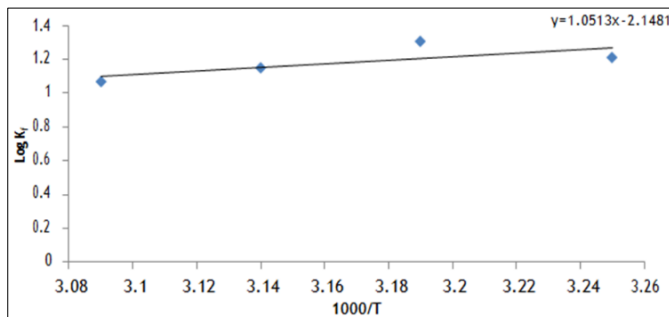


**Fig 5:** Molar conductance vs. mole-ratio plots for Benzo-18-crown-6-Ni<sup>2+</sup> in 50% (w/w) methanol at different temperatures

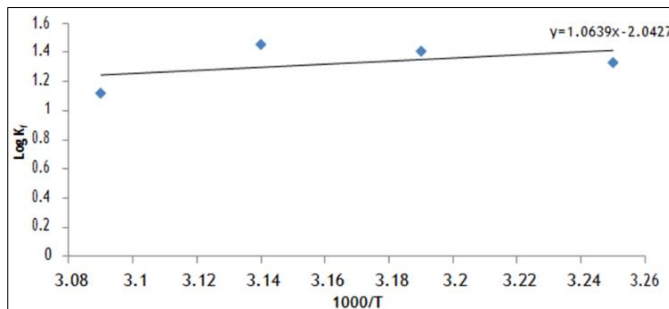
From the figures (1-5), all  $\log K_f$  versus  $1/T$  curves linearly increase with increase of temperatures (Izatt *et al.*, 1991) [10]. The increase in water content in the mixture should be expected to be accompanied by the increase in the hydrophobic hydration of crown ether molecules, while the increased organic solvent in the mixture will produce an increased solvation of nickel, cobalt and zinc cation.



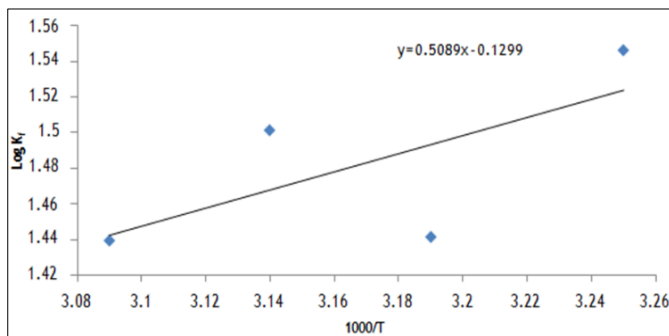
**Fig 6:**  $\log K_f$  vs.  $1/T$  plots for Benzo-18-crown-6-Ni<sup>2+</sup> complexes in 10% methanol at different temperatures.



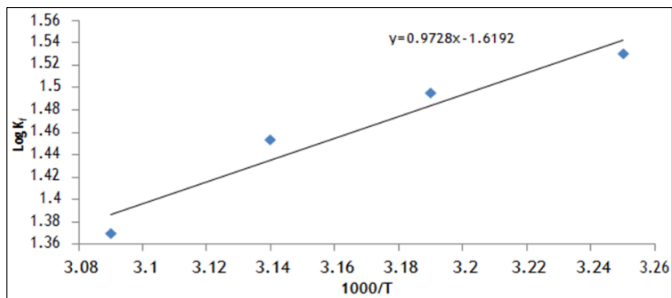
**Fig 7:**  $\log K_f$  vs.  $1/T$  plots for Benzo-18-crown-6-Ni<sup>2+</sup> complexes in 20% methanol at different temperatures.



**Fig 8:**  $\log K_f$  vs.  $1/T$  plots for Benzo-18-crown-6-Ni<sup>2+</sup> complexes in 30% methanol at different temperatures.

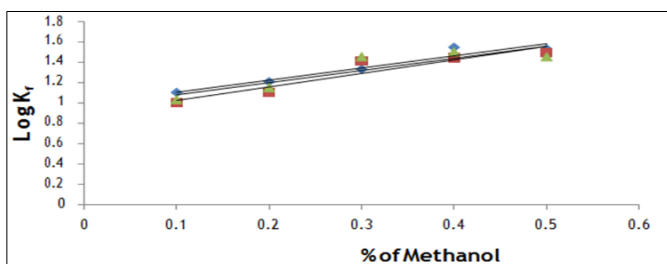


**Fig 9:**  $\log K_f$  vs.  $1/T$  plots for Benzo-18-crown-6-Ni<sup>2+</sup> complexes in 40% methanol at different temperatures.

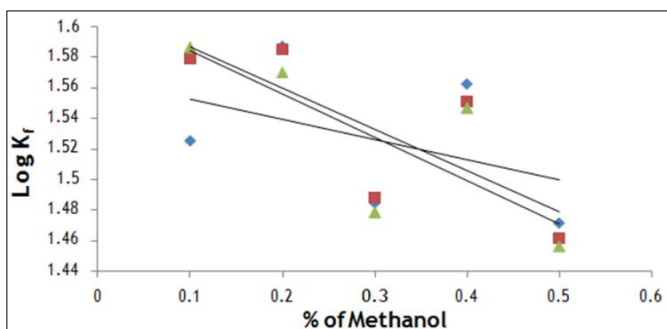


**Fig 10:** log  $K_f$  vs.  $1/T$  plots for Benzo-18-crown-6- $Ni^{2+}$  complexes in 50% methanol at different temperatures.

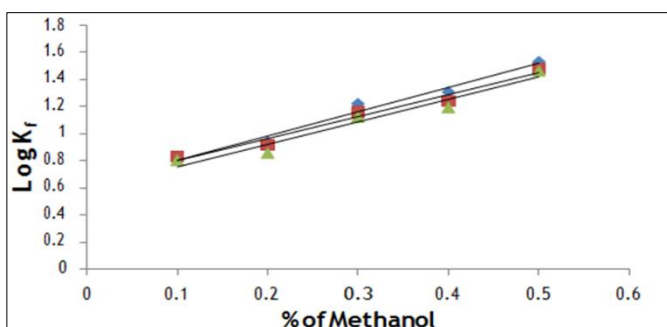
The van't Hoff plots of  $\log K_f$  versus  $1/T$  in all cases were linear and these plots are shown in Figures (6-10). These plots also applicable for  $Co^{2+}$  and  $Zn^{2+}$ .



**Fig 11:** Log  $K_f$  Vs. % of MeOH plots of MeOH-water solvent mixtures for  $Ni^{2+}$  at different temperatures.



**Fig 12:** Log  $K_f$  Vs. % of MeOH plots of MeOH-water solvent mixtures for  $Co^{2+}$  at different temperatures.



**Fig 13:** Log  $K_f$  Vs. % of MeOH plots of MeOH-water solvent mixtures for  $Zn^{2+}$  at different temperatures.

The plots for the changes of  $\log K_f$  versus the mole fraction of MeOH-water solvent mixtures at different temperatures (figures 11-13) show that the plots are found linear for  $Ni^{2+}$  and  $Zn^{2+}$  ion complexes and the  $K_f$  values increase with increase in organic portion of the solvent compositions. But the plots of  $Co^{2+}$  ion complexes (figure 12) are not linear and  $K_f$  values decrease with increase in organic portion. This behavior is probably due to metal ion and solvent interactions.

## Conclusions

The complexation reaction of  $Ni^{2+}$ ,  $Co^{2+}$  and  $Zn^{2+}$  ions with crown ether (benzo-18-crown-6) have been studied conductometrically in methanol-water mixed solvents at 308.15K, 313.15K, 318.15K, and 323.15K temperatures. The stability constants  $K_f$  of the resulting 1:1 complexes were determined. The kinetic stability of complexes refers to the speed with which transformation leading to the attainment of equilibrium will occur. The conductance behavior of  $Ni^{2+}$ ,  $Co^{2+}$  and  $Zn^{2+}$  and their complexes with crown ether have been studied in 10%, 20%, 30%, 40% and 50% MeOH-water mixed solvent at 308.15K, 313.15K, 318.15K, and 323.15K temperatures. The conductometric studies indicate the 1:1 complex formation between the studied metal ions and crown ether. From the conductometric results obtained on the thermodynamics of complexation of Benzo-18-Crown-6 with some transition metal ions in MeOH- water solvent mixtures are shown that the order of stability constants with studied all crown ethers is found to be  $Co(II) > Ni(II) > Zn(II)$ . Solvent illustrates the fundamental role in the  $M^{2+}$ -Benzo-18-crown-6 complexation reactions. Stability constants for  $Ni^{2+}$ ,  $Co^{2+}$  and  $Zn^{2+}$  with crown ether complexes in MeOH-water solvent compositions vary with the organic portion in the solvent mixtures. Thermodynamic parameters such as  $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$  for the complexation reactions are also considered. As  $\Delta G^0$  values are negative, the complexation reaction is spontaneous. The values of  $\Delta H^0$  are negative indicating that reactions are exothermic.  $\Delta S^0$  values are also negative. Thus the complex formations found to be thermodynamically stable. It is well known that the biological activity of many drugs can be enhanced upon complexing with metal ions. The biologically active compounds become more effective and bacterio-static upon complexation with metal ions. In the context of present research work, Benzo-18-crown-6 is used as ligand or chelating agent that contains oxygen atoms that can attach with metals or metal ions by coordinate linkages to form complexes. The biological activity of ligand is to be enhanced on complexing with metal ions, hence promoting their use in Pharmacology.

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