

## Complexation Study of 18-Crown-6 with Alkali Metal Ions in Ethanol + Water Binary Mixtures by Conductometric Technique and Assessment of Thermodynamic Parameters

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A conductometric investigation of the complexation of two alkali metal ions with 18-crown-6 has been performed in binary ethanol + water solvent mixtures at four different temperatures *viz.* 303.15 K, 308.15 K, 313.15 K and 318.15 K. The conductance analysis revealed that 18-crown-6 forms 1:1 complexes with alkali metal ions. The molar conductance of K<sup>+</sup> ion was higher than Na<sup>+</sup> ion but the stability constant followed the reverse order. For every case, the stability constant decreases with increasing temperature. The stability constants for the CE-Na<sup>+</sup> complexes followed the sequence 80% > 60% > 40% > 20% v/v at 303.15 K, while those for the CE-K<sup>+</sup> complexes were 80% > 40% > 60% > 20% v/v at the same temperature. Thermodynamic parameters revealed that the values of Gibb's free energy, enthalpy and entropy were negative, the spontaneity of the complexation process, exothermic in nature and thermodynamically favoured.

**Keywords:** 18-Crown-6, Alkali metal, Binary mixtures, Stability constant, Thermodynamic parameters, Conductometry.

### INTRODUCTION

Crown ethers represent a well-recognised group of host molecules within supramolecular chemistry. Since Pedersen discovered macrocyclic polyethers in 1967, these compounds have been thoroughly investigated for the ability to form complexes with metal ions (M<sup>n+</sup>) and numerous chemical species [1,2]. The formation of the DB18C6-potassium complex in 1967 was a turning point in crown ether chemistry [3]. Crown ethers can effectively coordinate with alkali and alkaline earth metals due to their structural characteristics, which include a hydrophilic cavity surrounded by a lipophilic framework [4-6]. In recent decades, significant experiment has been conducted on the complexation phenomenon of crown ethers (CEs) with M<sup>n+</sup> ions. Stability of CE-M<sup>n+</sup> complexes is governed by factors such as radius, cavity size, flexibility, solvent, *etc.* [7]. These factors must be considered when investigating a crown ether-metal ion complex. However, there has been relatively few researches on crown ethers with transition metal ion complexes [8-11].

Various techniques have been used to assess the stability constants of crown ether-metal ion complexes, including polarography [12-14], spectrometry [15-17], conductometry [18-20], potentiometry [21,22], fluorescence [23,24] and NMR [25-27] spectroscopy. Among these, conductometry represents a simple, inexpensive and efficient technique for determining complex formation and stability constants, particularly at low concentrations, while also demonstrating ionic mobility in solution [28]. The solvation of reactants significantly affects the complex formation and recent work has increasingly studied the influence of various solvents on the complexation of alkali metal ions with crown ethers through various analytical techniques [29-32]. In aqueous media, the majority of crown ethers exhibit complexes with lower selectivity and stability relative to those produced in less polar solvents. For example, whenever acetonitrile or methanol is used as a solvent instead of water, the stability of the complex formed between K<sup>+</sup> and 15-crown-5 is increased [31,33]. The Na<sup>+</sup> and K<sup>+</sup> complexes highlighted the complex dependency on the chemical properties of all ligands (18C6, 15C5, 12C4)

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and solvents (dioxane–water) mixture that was investigated by conductometric techniques [34].

The complexation of 24-crown-8 and 18-crown-6 with  $Zn^{2+}$  and  $Cu^{2+}$  in water–acetonitrile mixtures was recently investigated by Hossain *et al.* [35] using conductometry and reported a 1:1 complexation ratio. Similar results were also reported by Hoque *et al.* [36], who studied  $Zn^{2+}$  and  $Cu^{2+}$  complexation with benzo-18-crown-6 and benzo-15-crown-5 in DMF–water mixtures at different temperatures. They used molar conductivity data to calculate 1:1 stability constant, which showed the order  $Cu^{2+} > Zn^{2+}$ . The complexation of aza-18-crown-6 with  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  in acetonitrile–methanol mixtures at different temperatures was investigated conductometrically. The results showed that at 20 °C in pure acetonitrile, complex stability followed  $Zn^{2+} > Cu^{2+} > Co^{2+} \approx Ni^{2+}$ . However, the order was reversed when 20% methanol was added and further methanol addition decreased stability of the complexes [37]. Despite all of these advances, there remain relatively limited systematic studies for the solvation-controlled complexation of alkali metal ions with 18-crown-6 in ethanol–water mixtures.

On considering this, the current study uses precise conductometric measurements to evaluate the stability constants of  $Na^+$  and  $K^+$  complexes with 18-crown-6 in ethanol–water binary mixtures over a range of temperatures. Understanding the intrinsic ion selectivity of 18-crown-6 as well as the effects of temperature and solvent composition on complex stability, alongside associated thermodynamic parameters are the objectives of this study.

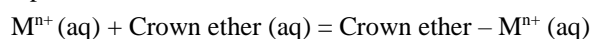
## EXPERIMENTAL

Analytical grade chemicals *viz.* 18-crown-6 (18C6), sodium chloride, potassium chloride and ethanol were procured from Merck, Germany. All reagents were of extra pure research grade and used without further purification. All the cleaning and solution-making process was carried out with the use of deionised water. Binary solvent mixtures of ethanol and water were prepared in different volume/volume (v/v) ratios of 20%, 40%, 60% and 80% by continuously adding the required volume of ethanol to water. The polarity and dielectric constant of the medium were systematically changed by these solvent compositions, which enabled the assessment of solvent effects on the complexation behaviour of 18C6 with sodium and potassium ions. The concentration of the crown ether (ligand) solution had been prepared at  $1.0 \times 10^{-4}$  M, whereas the metal salt solutions were prepared at a concentration of  $5.0 \times 10^{-3}$  M. In order to ensure the effective complex formation as well as avoid complications like precipitation, ion pairing or non-ideal solution behaviours, these concentration ranges have been chosen. The concentrations were achieved by dissolving the required quantities of ligand and salt in appropriate volumes of solvent that matched the desired compositions for the entire investigation.

**Conductometric procedure:** Conductometric measurements were conducted utilizing a Mettler Toledo conductivity meter equipped with a dip-cell of constant  $0.55 \text{ cm}^{-1}$ . Before each measurement, the equipment was calibrated with a 0.1 N KCl solution. A digital water bath (QC-WB100-2F) was

utilised for maintaining constant temperature conditions, allowing measurements at four different temperatures (303.15 K to 318.15 K) in 5 K intervals. In each experiment, 20 mL of a metal salt solution ( $5.0 \times 10^{-3}$  M) was poured into a glass test tube and adjusted in a thermostatically controlled water bath. After attaining thermal equilibrium, the initial conductivity of the metal ion solution was determined. The crown ether ligand solution was then added gradually with a precision micropipette. Following each addition, the conductivity of the resulting solution was assessed. The process continued with gradual additions of the ligand solution until the desired ligand-to-cation mole ratio was achieved.

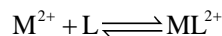
**Stability constant ( $K_f$ ):** For this, the metal ion  $M^{n+}$  (where  $n = 1, 2, 3, \dots$ ) interacts with the crown ether (*e.g.*, 18-crown-6) to create a CE– $M^{n+}$  complex, which can be generally represented as follows:



The stability constant ( $K_f$ ) of a complexation reaction indicates the equilibrium constant associated with the formation of the 18C6– $M^{n+}$  complex with the interaction of metal ion ( $M^{n+}$ ) to the crown ether (18-crown-6). The stability constant for 18-crown-6 can be expressed by the following:

$$K_f = \frac{[\text{18-crown-6-M}^{n+}]}{[M^{n+}][\text{18-crown-6}]}$$

Consider the following equation, which illustrates a standard complexation reaction between a metal ion ( $M^{2+}$ ) and a macrocyclic ligand (L):



$K_f$  can be expressed as the following equation:

$$K_f = \frac{[ML^{2+}]}{[M^{2+}][L]} \times \frac{f(ML^{2+})}{f(M^{2+})f(L)} \quad (1)$$

where  $f$  denotes the activity coefficient. In dilute solutions, the value of activity coefficient of the charge free ligand,  $f(L)$ , is frequently estimated to be 1.0. According to Debye-Huckel limiting law implies that  $f(M^{2+}) \approx f(ML^{2+})$  be summarised in order to cancel these two values in the equation. Consequently, it is possible to reduce the stability constant to the following expression:

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

where  $[ML^{2+}]$ ,  $[M^{2+}]$ ,  $[L]$  depict the equilibrium molar concentration of complex, free cation and free ligand, respectively.

Another alternative representation for the equation of the stability constant is given below:

$$K_f = \frac{[ML^{2+}]}{[M^{2+}][L]} = \frac{\Lambda_M - \Lambda_{\text{obs}}}{\Lambda_{\text{obs}} - \Lambda_{\text{ML}}[L]}$$

This study represents the molar conductivities of the metal ion–ligand complex and the free metal ion as  $\Lambda_{\text{ML}}$  and  $\Lambda_M$ , respectively. The molar conductivity of the solution during the titration is represented as  $\Lambda_{\text{obs}}$  and the concentration of the macrocyclic ligand (L) is marked by  $[L]$ .

The stability constant ( $K_f$ ) for the complexation reaction was determined utilizing the following equations [36,38,39]:

$$K_f = \frac{(\Lambda_M - \Lambda_{obs})(\Lambda_M - \Lambda_{ML})}{C_M \left\{ \frac{C_L}{C_M} (\Lambda_{obs} - \Lambda_{ML})(\Lambda_M - \Lambda_{ML}) - (\Lambda_{obs} - \Lambda_{ML})(\Lambda_M - \Lambda_{obs}) \right\}} \quad (2)$$

In this context, the symbols  $C_M$  and  $C_L$  signify the concentration of the salt and macrocyclic ligand (L), respectively.

## RESULTS AND DISCUSSION

**Variation in the molar conductivity ( $\Lambda_M$ ) of metal ion and crown ether mixtures in an ethanol-water media:** The molar conductance of crown ethers complexed with sodium(I) and potassium(I) chloride salts in various ethanol-water solutions was measured at the intervals of 5 K between 303.15 K and 318.15 K, exhibiting variations based on the mole ratio of ligand to metal ions. With multiple mole ratios,  $\Lambda_M$  values of  $M^{n+}$  ion + CE mixtures in ethanol + water mixed solvent are listed in Table-1.

TABLE-1  
MOLE RATIO *vs.* MOLAR CONDUCTANCE DATA  
FOR  $K^+$ -18-CROWN-6 COMPLEX IN 20% (v/v)  
ETHANOL AT DIFFERENT TEMPERATURES

Mole ratio	Molar conductance ( $\Lambda_M$ )			
	303.15 K	308.15 K	313.15 K	318.15 K
0	57.37	63.74	71.67	78.76
0.1	57.35	63.68	71.45	78.64
0.2	57.21	63.38	71.25	78.38
0.3	57.03	63.14	70.91	78.11
0.4	56.96	62.91	70.68	77.64
0.5	56.64	62.65	70.38	77.23
0.6	56.41	62.39	70.13	76.91
0.7	56.20	62.16	69.94	76.53
0.8	55.85	61.92	69.64	76.27
0.9	55.71	61.55	69.39	75.98
1.0	55.52	61.34	68.94	75.58
1.1	55.12	61.02	68.62	75.19
1.2	54.83	60.79	68.32	74.80
1.3	54.52	60.54	68.05	74.44
1.4	54.33	60.34	67.85	74.12
1.5	54.12	60.16	67.55	73.82
1.6	53.87	60.02	67.34	73.47
1.7	53.63	59.82	67.04	73.11
1.8	53.40	59.74	66.72	72.97
1.9	53.10	59.42	66.43	72.87
2.0	52.98	59.19	66.11	72.77
2.1	52.78	58.94	65.86	72.69
2.2	52.55	58.67	65.75	72.59
2.3	52.25	58.49	65.68	72.48
2.4	52.04	58.35	65.44	72.38
2.5	51.91	58.10	65.35	72.21
2.6	51.69	57.88	65.11	72.13
2.7	51.55	57.51	65.05	71.89
2.8	51.34	57.28	64.87	71.68
2.9	51.15	57.04	64.75	71.59
3.0	50.91	56.92	64.64	71.47

In each study, a gradual reduction in  $\Lambda_M$  was observed as the concentration of CEs increased. This outcome implies the mobility of CE +  $M^{n+}$  complexes is lower than that of free solvated  $M^{n+}$  ions. In every instance, the  $\Lambda_M$  values gradually

decrease as the CEs are inserted into the  $M^{n+}$  ion solution. The interaction of 1,10-diaza-18-crown-6 with various metal ions in the organic solvent mixture similarly exhibited this behaviour [40]. The complexation of  $Zn^{2+}$  and  $Cu^{2+}$  ions was also observed to exhibit this behaviour and their interaction with two CEs was studied at multiple temperatures in a range of DMF–water mixed solvents [36]. Even at mole ratios up to 3.5, the molar conductance *vs.* mole ratio plot declined in these cases to demonstrate a level-off tendency.

The plot of molar conductance *versus* mole ratio in the current investigation exhibited a tendency to level off as the mole ratios approached a value of 3. In several instances, a variation in the slopes was noted, implying the appearance of a 1:1 weak complex. The stability and selectivity of the formed complex are mostly determined by how well the size of the cation matches the cavity size of the crown ether [41]. The complexation of different crown ethers with  $Ag^+$  and  $Cu^{2+}$  ions with various cavity sizes and substituent groups revealed a reduction in molar conductivity as the mole ratio increased [42]. The idea of the larger CEs +  $M^{n+}$  complexes concerning the solvated  $M^{n+}$  ions may help clarify the decrease in molar conductivity values as the mole ratio of ligand to metal ions increases. In nearly all cases, molar conductivity exhibited a tendency to rise with increasing temperature. This phenomenon may be attributed to the enhanced ion mobility in solution with elevated temperatures. Fig. 1 depicts the representative molar conductivity ( $\Lambda_M$ ) *versus* ligand-to-metal mole ratio plots for  $K^+$  and  $Na^+$  ions at different temperatures.

**Stability constant ( $K_f$ ) for metal ions with crown ether complexes in ethanol + water media:** The value of the stability constant for a specific complex is a significant factor for observation since it provides crucial information regarding the stability of that complex. Therefore, in present study, the stability constants for the complexation of sodium and potassium ions with 18C6 crown ether were determined. The stability constants ( $K_f$ ) of  $M^{n+}$ +CE complexes in ethanol–water medium are shown in Table-2, which indicates that the solvent composition has a significant effect on complex stability.

The stability of the complexes demonstrated variability with the alteration of solvent percentage. However, the CE– $M^{n+}$  complexes showed an inconsistent pattern throughout the various compositions of the mixed solvent systems. As illustrated in Table-2, the variation of the  $\log K_f$  for the complexation of CE with  $Na^+$  and  $K^+$  ions followed the order: 18C6- $Na^+$  > 18C6- $K^+$ . The effectiveness of the complex and factors affecting the choice of a suitable host–guest pair are not solely determined by the comparative size of the metal ions and the encapsulation ability of the crown ether, but are significantly affected by solvent-dependent solvation and desolvation phenomena [43]. In a study of Inokuchi *et al.* [44], it emerged that the solvent effect substantially influences the ion selectivity, presumed due to free ions being less stable in methanol (having lower solvation energy) than in water. Another study showed that 18C6 exhibits a strong preference for  $K^+$  ions due to the optimal size matching and favourable solvation energy, particularly in aqueous solutions [45]. However, the difference in stability constants between  $K^+$  and  $Na^+$  with 18-crown-6 tends to decrease. The lower solvation energy of ethanol reduces the selectivity of

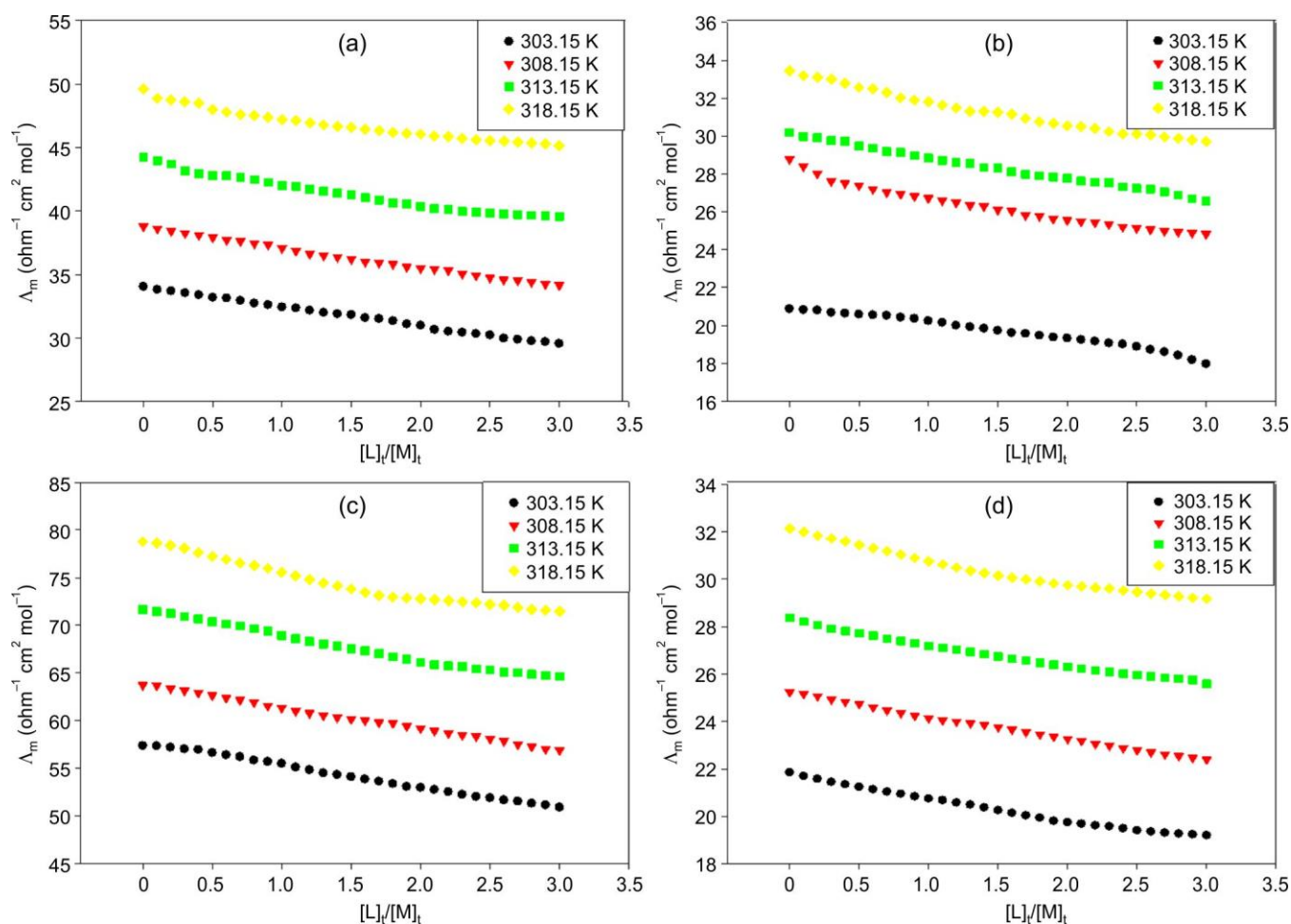


Fig. 1. Molar conductivity *versus* mole ratio plots for (a) 18C6-Na<sup>+</sup> ion complex in 40% (v/v) water + ethanol mixed medium, (b) 18C6-Na<sup>+</sup> ion complex in 80% (v/v) water + ethanol mixed medium, (c) 18C6-K<sup>+</sup> ion complex in 20% (v/v) water + ethanol mixed medium and (d) 18C6-K<sup>+</sup> ion complex in an 80% (v/v) water + ethanol mixed medium, at different temperatures

TABLE-2  
Log K<sub>f</sub> VALUES OF 18C6 WITH Na<sup>+</sup> AND K<sup>+</sup> COMPLEXES IN ETHANOL-WATER  
BINARY SOLVENT MIXTURES AT DIFFERENT TEMPERATURES

Sample	Crown ether	C <sub>EIOH</sub> % (v/v)	Log K <sub>f</sub> (mol L <sup>-1</sup> )			
			303.15 K	308.15 K	313.15 K	318.15 K
Na <sup>+</sup>	18C6	20	1.09	1.03	0.97	0.92
		40	1.10	1.03	0.96	0.88
		60	1.11	1.04	0.99	0.93
		80	1.18	1.13	1.06	1.01
K <sup>+</sup>	18C6	20	0.98	0.95	0.91	0.87
		40	1.08	1.04	0.95	0.89
		60	1.02	0.96	0.90	0.83
		80	1.10	1.04	0.96	0.91

K<sup>+</sup>, which in turn facilitates competition between Na<sup>+</sup> and K<sup>+</sup> for complexation with the crown ether. A further study has indicated that the Na<sup>+</sup> ion will occupy an asymmetrical position within the cavity, in closest proximity to three neighboring oxygens. This arrangement is intended to enhance convenient interactions between ions and etheric oxygen. This asymmetric arrangement allows H<sub>2</sub>O to establish a stronger hydrogen bond with oxygen on the ether and coordinate directly to Na<sup>+</sup>, compared to larger alkali ions [46]. A combination of solvation and structural factors demonstrates the higher stability

of Na<sup>+</sup> complexes in particular solvent compositions, despite the conventional size-fit preference to K<sup>+</sup>.

In this investigation, the stability constants of the CE-Na<sup>+</sup> complexes (Table-2) followed the order 80% > 60% > 40% > 20% at 303.15 K, whereas the stability constants of the CE-K<sup>+</sup> complexes followed the order 80% > 40% > 60% > 20% at the same temperature. The polarity of the solvent and the hydrogen-bonding properties of ethanol-water mixtures affect the solvation of free metal ions. Alkali metal ions usually form stronger and tightly packed solvation shells, causing

their desolvation more difficult compared to transition metal ions. They are less likely to form complexes with crown ethers as a result of their reduced desolvation tendency. Consequently, compared to alkali metal ions, transition metal ions exhibit a greater stability constant. Moreover, an obvious correlation between the cavity diameters and the ionic radii alone cannot be established since the divalent metal ions under study have very similar ionic radii. Consideration ought to be attributed to other elements including the degree of solvation, anionic effect, entropy changes, conformational changes, *etc.* [47]. The impact of temperature on  $\log K_f$  values was investigated for the complexation of CEs with  $M^{n+}$ . In all cases,  $\log K_f$  values were observed to decrease with increasing temperature. This suggests that the stability of the complexes may decline with the elevated temperatures.

**Thermodynamics of the crown ether +  $M^{n+}$  complexes in ethanol-water binary system:** Using the standard thermodynamic equations, the thermodynamic parameters for the complexation of crown ethers with metal ions were determined [48,49]:

$$\Delta G^\circ = -RT \ln K_f \quad (3)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

$$-RT \ln K_f = \Delta H^\circ - T\Delta S^\circ \quad (5)$$

$$\text{or } \ln K_f = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (6)$$

$$\text{or } \log K_f = -\frac{\Delta H^\circ}{2.303RT} + \frac{\Delta S^\circ}{2.303R} \quad (7)$$

In the above equations, R and T denote their standard physical meanings. By using eqn. 7, the value of enthalpy was calculated by determining the slope of the plot of  $\log K_f$  vs.  $1/T$ . Various  $\log K_f$  vs.  $1/T$  plots are shown in Fig. 2. The linear relationship observable in the  $\log K_f$  against  $1/T$  graphs, with  $R^2$  values exceeding 0.97 (Fig. 2a-d), allowed for the utilisation of a singular slope and intercept from each graph for determining the  $\Delta H^\circ$  and  $\Delta S^\circ$  values.

Tables 3 and 4 illustrate the thermodynamic properties,  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ , associated with the complexation process. The values of  $\Delta G^\circ$  were found to be negative, indicating the spontaneous formation of the complexation reaction. In a NaCl solution, the Gibb's free energy change ( $\Delta G^\circ$ ) values for the complexes formed between 18C6 and  $\text{Na}^+$  ions were observed to be relatively higher compared to those formed between 18C6 and  $\text{K}^+$  ions, for compositions of 20%, 40% and 80% of the ethanol-water binary solvent system. However, the Gibb's

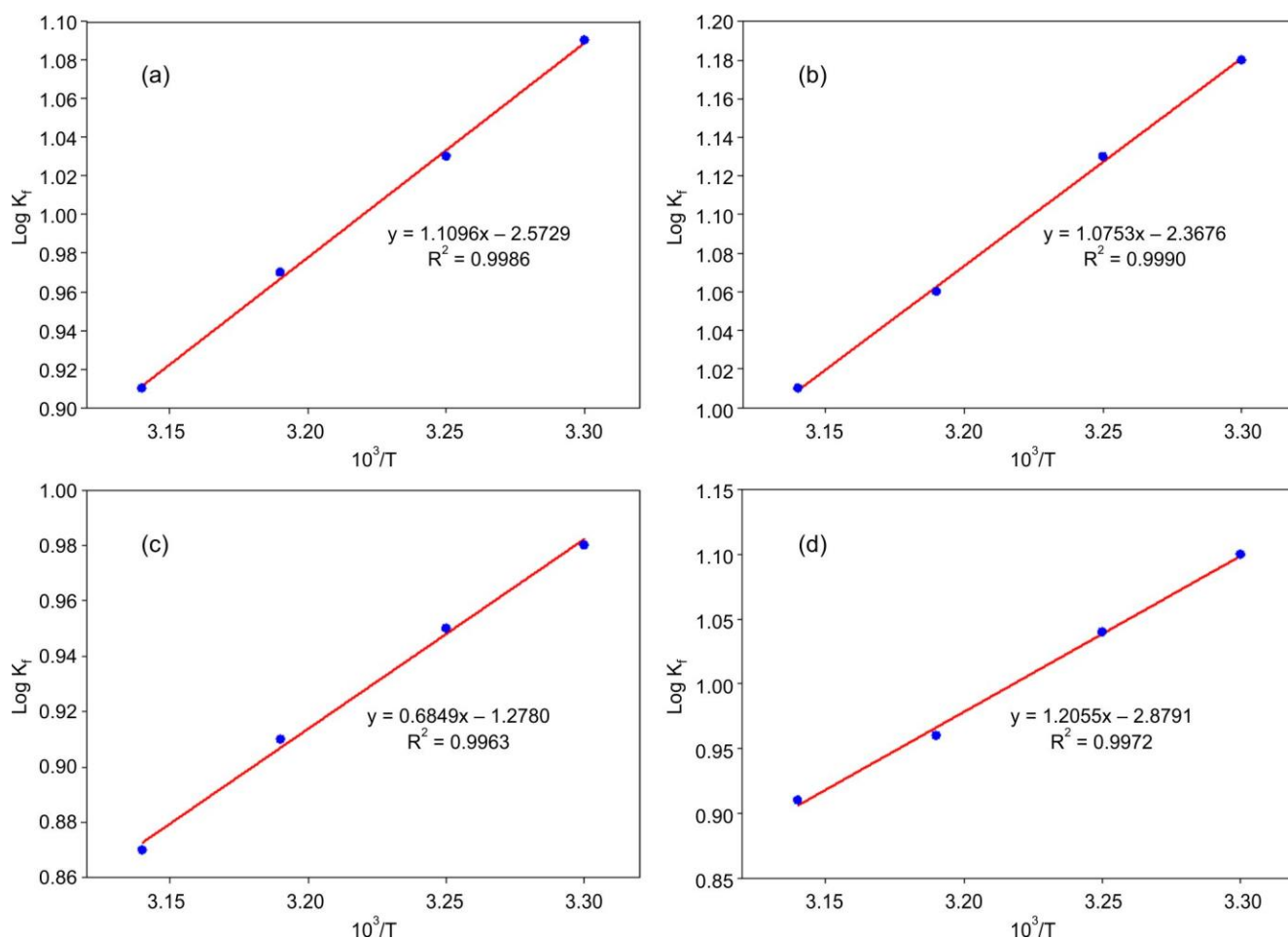


Fig. 2. The  $\log K_f$  versus  $1/T$  plots for (a) complexation of 18C6 with  $\text{Na}^+$  in 20% (v/v) water + ethanol mixed solvent, (b) complexation of 18C6 with  $\text{Na}^+$  in 80% (v/v) water + ethanol mixed solvent, (c) complexation of 18C6 with  $\text{K}^+$  ion complex in 20% (v/v) water + ethanol mixed solvent and (d) complexation of 18C6 with  $\text{K}^+$  ion complex in 80% (v/v) water + ethanol mixed solvent

TABLE-3  
THERMODYNAMIC PARAMETERS ( $\Delta G^\circ$ ,  $\Delta H^\circ$  AND  $\Delta S^\circ$ ) VALUES FOR  
18-CROWN-6- $\text{Na}^+$  COMPLEX IN ETHANOL-WATER SOLVENT MIXTURES

Ligand	Solvent	Composition	$\Delta G^\circ$ (KJ mol <sup>-1</sup> )	$\Delta H^\circ$ (KJ mol <sup>-1</sup> )	$\Delta S^\circ$ (J K <sup>-1</sup> mol <sup>-1</sup> )
18-crown-6	Ethanol	20%	-6.33	-21.25	-49.26
		40%	-6.38	-25.84	-64.19
		60%	-6.44	-20.85	-47.66
		80%	-6.85	-20.59	-45.33

TABLE-4  
THERMODYNAMIC PARAMETERS ( $\Delta G^\circ$ ,  $\Delta H^\circ$  AND  $\Delta S^\circ$ ) VALUES FOR  
18-CROWN-6- $\text{K}^+$  COMPLEX IN ETHANOL-WATER SOLVENT MIXTURES

Ligand	Solvent	Composition	$\Delta G^\circ$ (KJ mol <sup>-1</sup> )	$\Delta H^\circ$ (KJ mol <sup>-1</sup> )	$\Delta S^\circ$ (J K <sup>-1</sup> mol <sup>-1</sup> )
18-crown-6	Ethanol	20%	-5.69	-13.11	-24.47
		40%	-6.27	-23.47	-56.63
		60%	-6.92	-22.29	-54.03
		80%	-6.38	-23.08	-55.13

energy value of the sodium complexes (*i.e.* 18C6 +  $\text{Na}^+$ ) was observed to be relatively lower than that of the  $\text{K}^+$  ion complexes (*i.e.* 18C6 +  $\text{K}^+$ ) for a composition of 60% ethanol-water binary solvent mixture. Furthermore, by using the proportion of the ethanol-water binary solvent system extensively, a increasing tendency for negative values of  $\Delta G^\circ$  was obtained for the complexation process of specific crown ether with a studied metal ion (Tables 3 and 4). With a few exceptions (60% composition for KCl, which was very large), this shows an increasing spontaneous behaviour of complexation process at a greater proportion of the ethanol-water binary solvent system. The  $\Delta H^\circ$  values for the 18C6- $\text{Na}^+$  and 18C6- $\text{K}^+$  complexes were constantly negative at all temperatures and compositions of solvent investigated. This signifies that the complexation reaction is exothermic in nature. In each composition, the values of  $\Delta S^\circ$  for CE +  $\text{Na}^+$  and CE +  $\text{K}^+$  are negative, indicating that the complexation reaction is thermodynamically favourable. A possible reason for the negative entropy is a decline of conformational flexibility as crown ethers move from a flexible uncomplexed form to a more rigid configuration during complexation to metal ions [50]. In addition, as solvent molecules that have been displaced from the free ions and crown ether become more structured around the complex that is formed, solvent reorganisation plays an important role in the negative entropy change [50]. However, the negative values of  $\Delta H^\circ$  and  $\Delta S^\circ$  for 18C6 +  $\text{K}^+$  ion complexes are smaller than those for 18C6 +  $\text{Na}^+$  in 20% and 40% (v/v) ethanol + water binary systems, but the reverse results were obtained for 60% and 80% (v/v) ethanol + water media.

## Conclusion

The selectivity of crown ethers is mostly due to the size-fit principle, where a stable complex form with the cation whose ionic radius nearly matches the size of the cavity of the crown ether. The present findings demonstrate that the selectivity of crown ethers for metal cations in solution is influenced not only by size compatibility but also significantly by the properties of the solvent. The findings of this study demonstrate that the stability pattern of 18C6 complex with the investigated metal cations ( $\text{Na}^+$  and  $\text{K}^+$ ) can be affected by the com-

position of the mixed solvent system. These results suggest the potential for alterations in stability and, consequently, changes in the selectivity of the ligands that may be obtained in specific mixed solvent systems. Consequently, it is not reasonable to anticipate a linear correlation between these parameters ( $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ ) and the solvent composition of these mixed solvents system. The thermodynamic behaviour of CE-metal ion complexes in specific binary mixed solvents often deviates from monotonicity. This can be rationalised by considering the strong solvent-solvent interactions that modify their individual properties and impact the solvation and stabilisation of the complexes.

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## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

## DECLARATION OF AI-ASSISTED TECHNOLOGIES

During the preparation of this manuscript, the authors used an AI-assisted tool(s) to improve the language. The authors reviewed and edited the content and take full responsibility for the published work.

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