

Thermodynamic Parameters for the Complexation of 18-Crown-6 with Ag⁺, Pb²⁺, Cd²⁺, Cu²⁺, Co²⁺ and Ni²⁺ in Methanol - Water Solvents by Conductometry

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ABSTRACT. The complexation of 18-crown-6 with Ag⁺, Pb²⁺, Cd²⁺, Cu²⁺, Co²⁺ and Ni²⁺ in methanol-water solvents has been studied using a conductometric technique. Log K, ΔH⁰ and ΔS⁰ values are determined in 0% - 90 w% methanol-water at several temperatures in the range 288 - 308K. The measured stability constants and thermodynamic parameters were found to be solvent dependent. There is an inverse relationship between the stability constants of the complexes and Gutmann donicity of the solvents. The measured molar conductivities, Λ, of Pb²⁺, Ag⁺, and Cd²⁺ complexes of 18-crown-6, were observed to decrease significantly for mole ratios, [L]₀/[Mⁿ⁺]₀, close to unity while those of Cu²⁺, Co²⁺, and Ni²⁺ complexes were decreased less significantly. The measured molar conductivities have been analysed using a 1:1 stoichiometric model. The stability constant, K, and the limiting molar conductivity, Λ_c, for each 1:1 complex have been determined from the measured molar conductivities by using a non-linear least-squares analysis. In 90% methanol-water solvents used, the binding sequence, based on the value of log K at 298 K, was found to be Pb²⁺ > Ag⁺ > Cd²⁺ > Cu²⁺ > Co²⁺ > Ni²⁺. The significance of the determined values of the present thermodynamic parameters has been discussed in terms of solvent medium and relative sizes of cations and crown ether cavity.

The interest in complexation reactions between crown ethers and metal cations has increased considerably since Pedersen's preparative work (Pedersen 1967). The stability of these complexes is governed by a number of factors such as solvent medium, the relative sizes of the cation and the crown ether cavity, the flexibility of the crown ether and the number of donor atoms in the crown ether ring. These

factors have been investigated by many workers (Izatt *et al.* 1976, Frensdorff 1971, Takeda 1979, Takeda and Goto 1979) using different techniques in order to understand the complexation process by determining stability constants and thermodynamic parameters. The importance of these thermodynamic determinations can be seen from the huge number of reported data in this field of chemistry which are reviewed by Izatt *et al.* (1985, 1991).

Izatt *et al.* (1976, 1977) and Lamb *et al.* (1980) have used a calorimetric method to obtain thermodynamic parameters for the complexation of Ag^+ and Pb^{2+} with 18-crown-6 in water, methanol and methanol-water solvents at 298 K. Frensdorff (1971) used a potentiometric method for obtaining the stability constant of 18-crown-6 with Ag^+ in water. Kolthoff and Chantooni (1980) have used an ion-selective electrode technique to obtain the stability constant for the binding of 18-crown-6 with Ag^+ in methanol. Thermodynamic data have been determined for the complexation of Ag^+ with 18-crown-6 in methanol by conductometry (Lee *et al.* 1990) and calorimetry (Buschmann 1985). Luca *et al.* (1985) used polarography, and Brighli *et al.* (1985) used an ion-selective electrode method to determine aqueous stability constants at 298 K for the binding of Pb^{2+} with 18-crown-6. A number of workers have determined stability constants in methanol for the complexation of Pb^{2+} with 18-crown-6 using calorimetry (Buschmann 1985), ion-selective electrode (Buschmann 1986) and polarography (Buschmann 1985). Kulstad and Malmsten (1981) obtained stability constants in water for the complexation of Cd^{2+} , Pb^{2+} , and Ag^+ with 18-crown-6 using potentiometry while Luca *et al.* (1985) determined the aqueous stability constant for 18-crown-6 complex of Cd^{2+} using polarography. Arnaud-Neu *et al.* (1977) and Spiess *et al.* (1980) have used potentiometry to obtain stability constants for the binding of Cd^{2+} with 18-crown-6 in water and methanol.

In a previous paper (Sway and Abushamleh 1995), we have reported thermodynamic parameters for the complexation of dibenzo-18-crown-6 with Ag^+ , Pb^{2+} , and Cd^{2+} in acetonitrile-water solvents in the temperature range 288-308 K using a conductometric method. The present study was carried out to determine $\log K$, ΔH° and ΔS° values for the complexation of 18-crown-6 with Ag^+ , Pb^{2+} , Cd^{2+} , Cu^{2+} , Co^{2+} and Ni^{2+} cations in water and methanol-water solvents by a conductometric technique in order to study the factors influencing complex formation such as solvent medium and cation size.

Experimental

18-Crown-6 (99% purity) was obtained from Janssen Chimica and used without further purification. The following salts were obtained from the indicated suppliers:

Ag NO₃ (99.5%, Degussa AG), Pb (NO₃)₂ (99%), Cd (NO₃)₂ · 4H₂O (> 99.9%), Ni (NO₃)₂ · 6H₂O (99%), Reidel-De Haen AG, Cu(NO₃)₂ · 3H₂O (98%) and Co(NO₃)₂ · 6H₂O (> 99%), Fluka AG. Methanol 99.8%, AR, C.B.H Lab Chemicals) was used as supplied as the solvent for the crown ether. Boiled deionized water was used as the solvent for all metal nitrate salts. The solvents were prepared from measured weights of methanol and boiled, deionized water. Salt solutions of ca. 4 x 10⁻⁴ M were prepared by dissolving the appropriate weight of each metal salt in the methanol-water solvents. Similar solutions with the same total salt concentration, were also used as solvents in the preparation of the 18-crown-6 solutions. All solutions were protected from light.

Potassium chloride (99.5%, Harris Reagent) was used for determining the cell constant and for checking the accuracy of the conductivity meter. The conductance measurements were conducted on a Microprocessor Conductivity Meter, Model WTW/LF 537, equipped with a conductivity cell, model WTW/Tetracon 96, with cell constant of 0.609 cm⁻¹. The temperature of the reaction was controlled to only ± 0.1 °C using a thermostated circulator water bath (HAAKE D8) equipped with a refrigeration unit. In a typical run, 50 ml of a metal nitrate solution was placed in a stoppered water-jacketed glass cell (150 ml) connected to the thermostated water bath maintained at the desired temperature and equipped with a magnetic stirrer. The stoper has two inlets, one to fit the conductivity cell and the other to allow the addition of small increments of crown ether. The conductivity of the crown ether-free salt solution was measured after thermal equilibrium has been reached: within 15 min. 0.50 ml increments of 18-crown-6 solution (ca. 8 x 10⁻³ M), with the same salt concentration as that of the initial metal salt solution, were delivered by means of a pipette. The conductivity of the reaction mixture was then recorded after stirring. Addition of the crown ether solution was continued until the desired amount was achieved and the variation in conductivity is negligible. In all experiments the residual conductivity of methanol- water solvents was measured under the same conditions of the experiment and subtracted from that obtained for a studied solution.

Results and Discussion

In this study the 1:1 complexation of a metal cation, Mⁿ⁺ (Mⁿ⁺ = Ag⁺, Pb²⁺, Cd²⁺, Cu²⁺, Co²⁺ and Ni²⁺); with 18-crown-6, L, is assumed. The equilibrium equation for the complexation process is given by



According to eqn. (I), the stability constant, K , of the formed complex is given by

$$K = \frac{[ML^{n+}]}{[M^{n+}][L]} \quad (1)$$

where $[ML^{n+}]$, $[M^{n+}]$ and $[L]$ are the molar concentrations of the complex uncomplexed metal cation and uncomplexed crown ether, respectively. Under our experimental conditions (dilute solutions), it is assumed that the ratio of activity coefficients is unity (eqn. I). According to eqn. (I), the following concentration terms are defined by the following expressions

$$[M^{n+}] = \alpha [M^{n+}]_0 \quad (2)$$

$$[ML^{n+}] = (1 - \alpha) [M^{n+}]_0 \quad (3)$$

$$[L] = [L]_0 - (1 - \alpha) [M^{n+}]_0 \quad (4)$$

where $[M^{n+}]_0$, $[L]_0$ and α are the molar concentrations of total metal cation, total 18-crown-6, and the degree of dissociation of the complex, respectively. The observed conductivity, κ , of the resulted solution due to the addition of the crown ether to the metal cation is written as

$$\kappa = \kappa_0 + \kappa_c \quad (5)$$

where κ_0 and κ_c are the conductivities of the free metal salt and the complexed metal salt, respectively. The observed molar conductivity, Λ ($S \text{ cm}^2 \text{ mol}^{-1}$) of the resulting solution is given by the expression

$$\Lambda = 1000 \kappa / [M^{n+}]_0 \quad (6)$$

The details of the method of calculation have been reported previously (Sway and Abushamleh 1995).

In the first series of experiments 18- crown-6 was allowed to interact with Pb^{2+} cation in H_2O , 50%, 70% and 90% methanol at several temperatures between 288 K and 308 K. Typical results are plotted in Fig. 1 as Λ vs. $[L]_0/[Pb^{2+}]_0$. These plots show appreciable decrease of Λ with an increase in 18- crown-6 concentration. The slopes of these curves change significantly at the point when the ratio $[L]_0/[Pb^{2+}]_0$ is close to unity, indicating that the 18- crown-6 forms a 1:1 complex with Pb^{2+} cation.

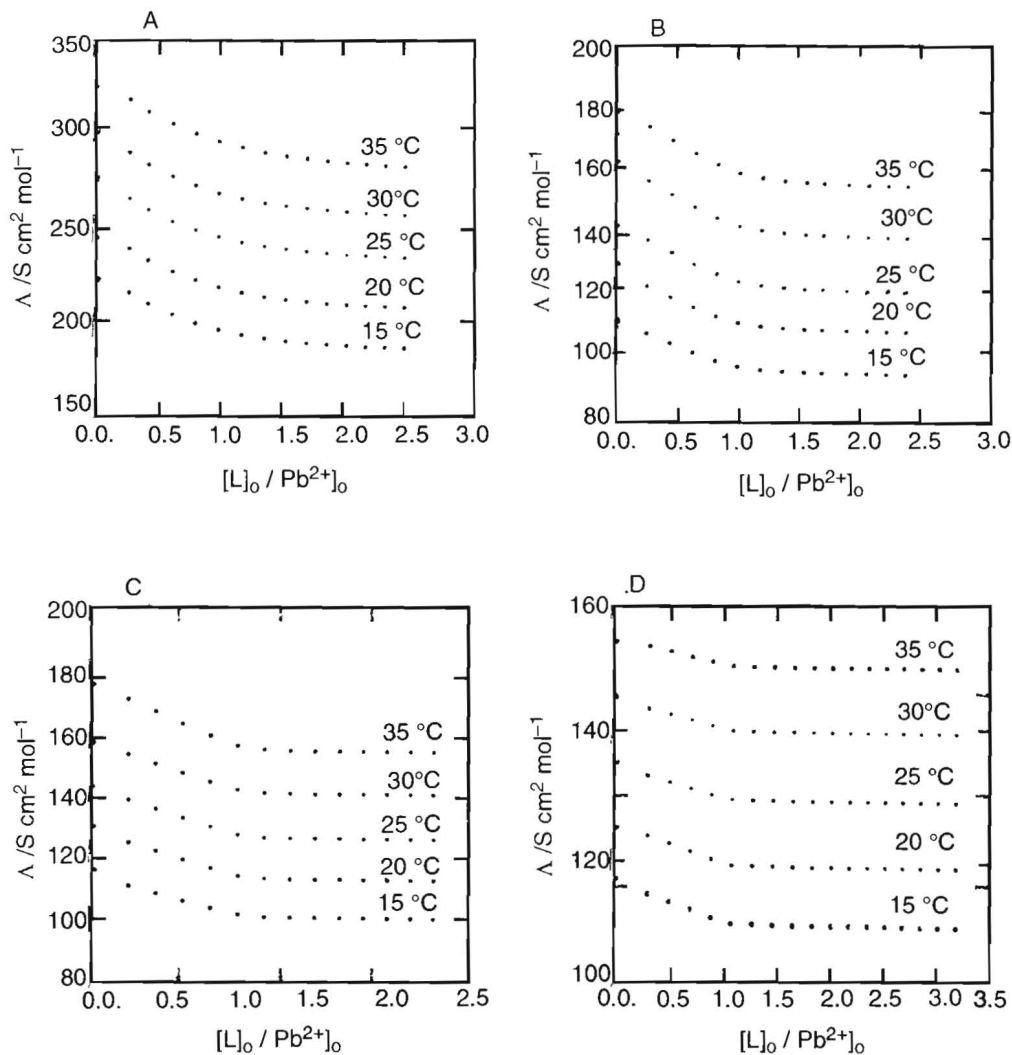


Fig. 1. Λ vs. $[L]_0/[Pb^{2+}]_0$ for the complexation of 18-crown-6 with Pb^{2+} in A, H_2O ; B, 50%; C, 70%; and D, 90% methanol. $[Pb^{2+}]_0$: A, 3.577×10^{-4} ; B, 3.582×10^{-4} ; C, 3.614×10^{-4} ; and D, $3.634 \times 10^{-4} \text{ mol dm}^{-3}$.

In the second series of experiments, 18-crown-6 was added step-by-step to interact with Ag^+ cation in H_2O , 50%, 70% and 90% methanol. Typical results of this system are shown in Fig. 2. The Λ vs. $[\text{L}]_0/[\text{Ag}^+]_0$ plots in Fig. 2 C show relatively more decrease of Λ than those in Fig. 2 A-B with an increase in the concentration of the crown ether when the ratio $[\text{L}]_0/[\text{Ag}^+]_0$ is close to unity except for the interaction of the crown ether with Ag^+ cation in H_2O where there is slight decrease in Λ (Fig. is not shown here).

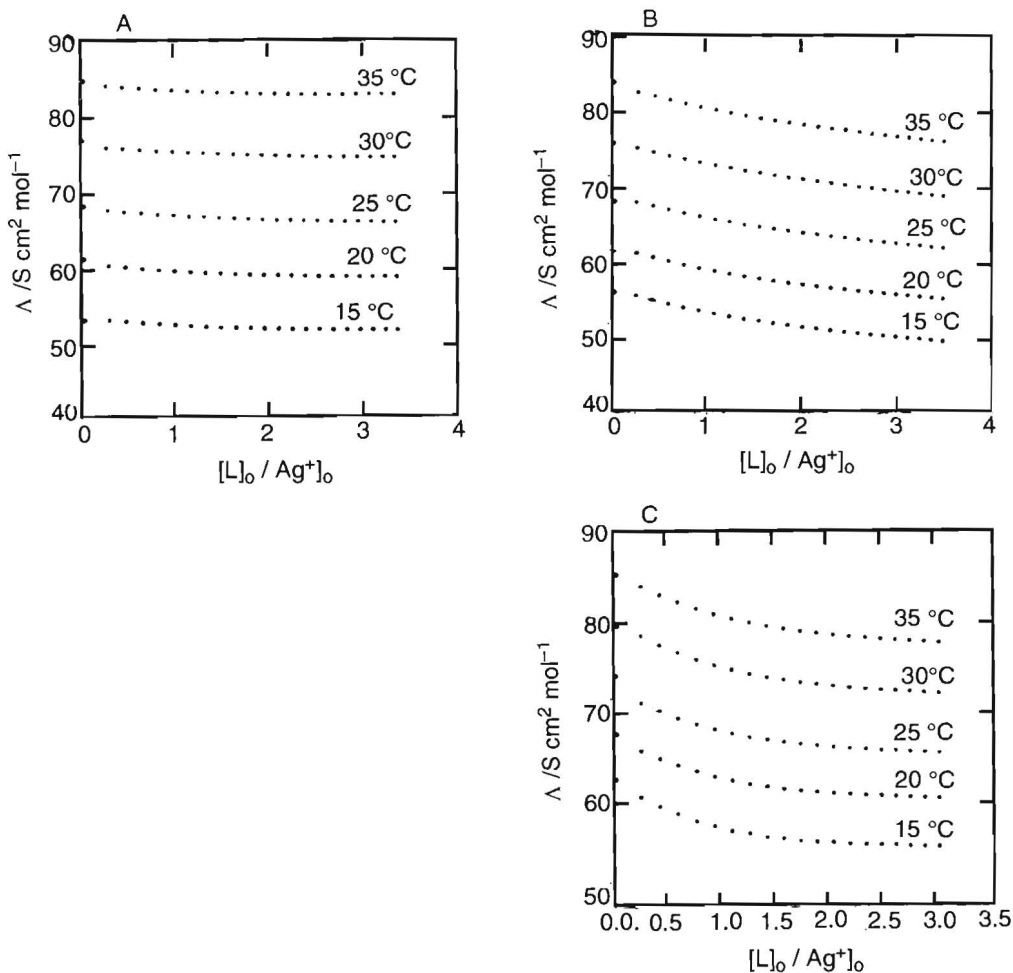


Fig. 2. Λ vs. $[\text{L}]_0 / [\text{Ag}^+]_0$ for the complexation of 18-crown-6 with Ag^+ in A, 50%; B, 70%; and C, 90%; methanol. $[\text{Ag}^+]_0$: A, 3.867×10^{-4} ; B, 3.874×10^{-4} ; and C, 3.912×10^{-4} ; mol dm^{-3} .

The third series of experiments were carried out in which Cd^{2+} cation was allowed to interact with 18-crown-6 in 70% and 90% methanol. Typical results of these experiments are shown in Fig. 3.

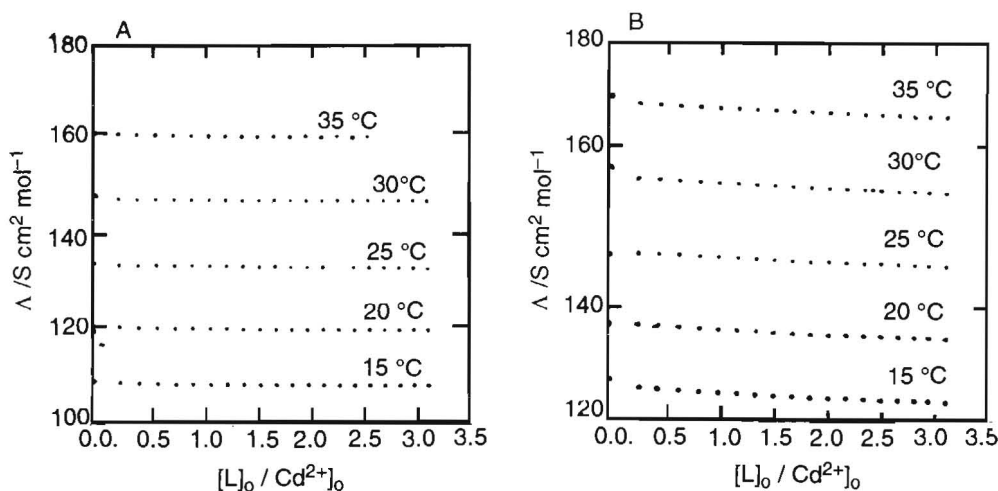


Fig. 3. Λ vs. $[\text{L}]_0 / [\text{Cd}^{2+}]_0$ for the complexation of 18-crown-6 with Cd^{2+} in A, 70% and B, 90% methanol. $[\text{Cd}^{2+}]_0$: A, 3.964×10^{-4} ; and B, 3.950×10^{-4} mol dm^{-3} .

The slopes of these curves are smaller than those of Pb^{2+} - 18-crown-6 complex. In the fourth series of experiments, 18-crown-6 was added to Cu^{2+} , Co^{2+} and Ni^{2+} cations in 90% methanol. The obtained results are shown in Fig. 4. The slopes of these curves are much smaller than those of other studied cations in 90% methanol. Another series of experiments were carried out in 70% methanol for the interaction of 18-crown-6 with Co^{2+} , Ni^{2+} and Cu^{2+} . The obtained results of these experiments show negligible decrease in molar conductivity as the concentration of the crown increases. So it was impossible to determine the stability constants for these systems. The results obtained in this study (Fig. 1-4) were used to determine K and Λ_c values.

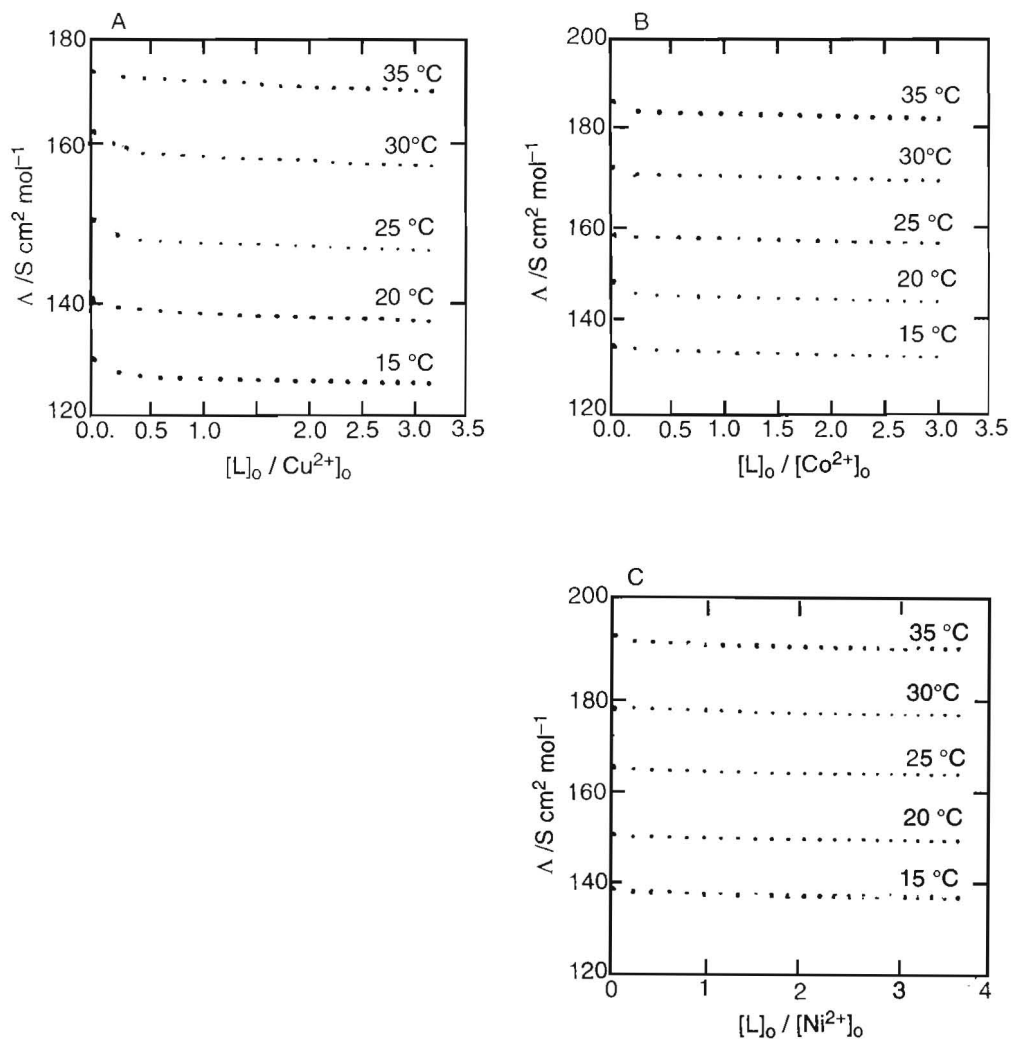


Fig. 4. Λ vs. $[L]_0/[M^{2+}]_0$ for the complexation of A, Cu^{2+} ; B, Co^{2+} and C, Ni^{2+} with 18-crown-6 in 90% methanol. $[\text{Cu}^{2+}]_0$: A, 3.916×10^{-4} ; $[\text{Co}^{2+}]_0$: B, 3.923×10^{-4} ; $[\text{Ni}^{2+}]_0$: C, $3.949 \times 10^{-4} \text{ mol dm}^{-3}$.

Stability constants of complex formation, K , were calculated to determine thermodynamic parameters ΔH° and ΔS° . The present results show that K decreases as the temperature is increased indicating that the complexation of the studied cations with 18-crown-6 is an exothermic process. Using the mean values of K , ΔH° and ΔS° values were determined from the plot of $\log K$ vs. $1/T$ by applying a linear-least-squares method according to the relation

$$\log K = - \Delta H^\circ / 2.303 RT + \Delta S^\circ / 2.303 R \quad (7)$$

These plots are linear as suggested by eqn. (7) (Fig. 5). Values of $\text{Log } K$, ΔH° and ΔS° together with literature values at 298 K are summarized in Table. 1. The error limits quoted for ΔH° and ΔS° were 95% confidence limits with correlation coefficients > 0.98 .

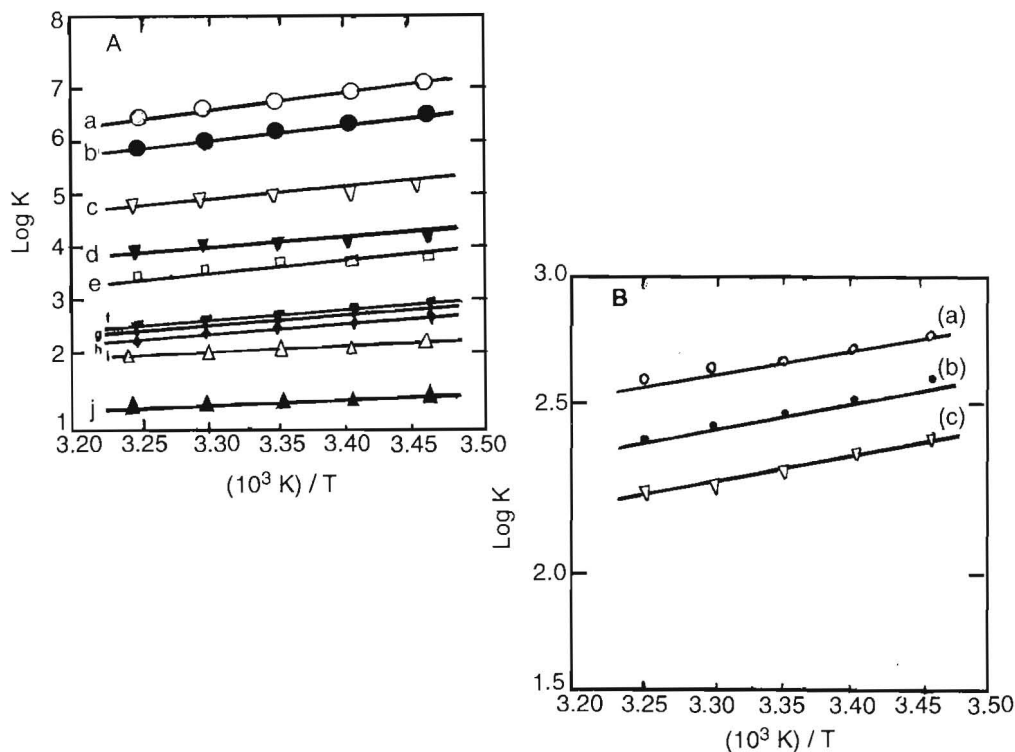


Fig. 5. $\text{Log } K$ vs. $1/T$ for the 1:1 complexation of Ag^+ , Pb^{2+} , Cd^{2+} , Cu^{2+} , Co^{2+} and Ni^{2+} with 18C6 in different methanol-water solvents. A: (a)–(d) Pb^{2+} ; (a) 90%, (b) 70%, (c) 50% CH_3OH , (d) H_2O . (e)–(f), (i), (j) Ag^+ ; (e) 90%, (f) 70%, (i) 50%, (j) H_2O . (g)–(h) Cd^{2+} ; (g) 90%, (h) 70% CH_3OH . B: (a)–(c) 90% CH_3OH ; (a) Cu^{2+} ; (b) Co^{2+} ; (c) Ni^{2+} .

Table 1 shows that literature values of ΔH° and ΔS° for the complexation of 18-crown-6 with Ag^+ , Pb^{2+} , Cd^{2+} , Co^{2+} and Ni^{2+} cations in methanol- water solvents are unavailable except those reported by Izatt and *et al.* (1976) for Pb^{2+} in 70% methanol- water at 298 K using calorimetric technique. The reported data by Izatt *et al.* (1976) for the complexation of Pb^{2+} in 70% methanol are comparable with those obtained in this study. On the other hand, it is unjustifiable to compare other literature data obtained in methanol with our data determined in methanol- water solvents. Values of Log K , ΔH° and ΔS° are available in the literature for the complexation of Ag^+ and Pb^{2+} cations with 18-crown-6 in aqueous medium at 298 K using different techniques. The aqueous thermodynamic parameters obtained in this study for the complexation of Pb^{2+} and Ag^+ cations are comparable with those reported by Izatt *et al.* (1976) using calorimetry. The aqueous log K value obtained in this study for the complexation of Ag^+ with 18-crown-6 at 298 K is also comparable with that determined by Izatt *et al.* (1976) using calorimetry but it is lower than the one determined by Frensdorff (1971) using potentiometry (Table 1).

The present results for the complexation of Ag^+ , Pb^{2+} and Cd^{2+} with 18-crown-6 summarized in Table 1 show that the change in solvent composition from water to methanol- water mixtures results in appreciable increase in the values of Log K , ΔH° and ΔS° . The results given in Table 1 show the influence of solvents on the complexation process involving macrocyclic ligands and metal ions. This may be attributed to a decrease in polarity and dielectric constant of methanol- water mixtures. Furthermore, the stability of the complexes increases with decreasing solvating power of the solvents as expressed by the Gutmann donor number (Gutmann and Wyche 1966). Since the donor number of methanol ($\text{DN} = 19.7$) is smaller than that of water ($\text{DN} = 33.0$), this indicates that methanol shows less competition with the ligand molecules for metal ions which in turn results in more stable complexes (Kashanian and Shamsipur 1989). This is in accord with the Log K values obtained in aqueous and methanol solvents. Based on the above observation, the results obtained in this study show that as the proportion of methanol increases the donor number of the mixed solvents decreases and consequently the stability of the complexes formed increases. Similar observation was obtained in case of ΔH° and ΔS° in which the magnitudes of these parameters become more negative as the proportion of methanol increases (Table 1).

The log K , ΔH° and ΔS° values obtained in the present work for the complexation of 18-crown-6 with the cations studied in aqueous medium suggest the following selectivity order: $\text{Pb}^{2+} \gg \text{Ag}^+$ and in case of 90% methanol the stability sequence is $\text{Pb}^{2+} > \text{Ag}^+ > \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+}$ (Table 1).

Table 1. Stability constants and thermodynamic quantities of the 1:1 complexes of 18-crown-6 with Ag⁺, Pb²⁺, Cd²⁺, Cu²⁺, Co²⁺ and Ni²⁺ in methanol- water solvents at 298 K

Cation	Solvent	Log K	-ΔH° / kJ mol ⁻¹	-ΔH° / kJ ⁻¹ mol ⁻¹	ΔH° / TΔS°	Method*	Reference
Ag ⁺	H ₂ O	1.49 ± 0.02	9.13 ± 0.95	2.02 ± 0.04	15.17	Cond.	This Work
	H ₂ O	1.60	-	-	-	Pot.	Frensdorff (1971)
	H ₂ O	1.50	9.07	1.70	17.9	Cal.	Izatt <i>et al.</i> (1976)
	H ₂ O	1.24	-	-	-	Cond.	Shen <i>et al.</i> (1984)
	(50% CH ₃ OH)-H ₂ O	2.45 ± 0.04	16.35 ± 1.13	8.62 ± 0.60	6.36	Cond.	This Work
	(70% CH ₃ OH)-H ₂ O	2.95 ± 0.05	23.22 ± 1.62	21.51 ± 2.30	3.62	Cond.	This Work
	(90% CH ₃ OH)-H ₂ O	3.85 ± 0.02	34.40 ± 1.85	41.80 ± 2.10	2.76	Cond.	This Work
	CH ₃ OH	4.58	38.70	40.70	3.19	Cal.	Izatt <i>et al.</i> (1977), Lamb <i>et al.</i> (1980)
	CH ₃ OH	4.57	-	-	-	ISE	Kolthoff (1980)
	CH ₃ OH	4.60	40.90	57.50	2.39	Cond.	Lee <i>et al.</i> (1990)
	CH ₃ OH	4.58	39.10	-44.00	2.98	Cal.	Buschmann (1985)
	CH ₃ OH	4.65	-	-	-	Pot.	Buschmann (1985)
	Pb ²⁺	H ₂ O	4.23 ± 0.02	21.95 ± 1.73	-9.15 ± 0.63	-8.05	Cond.
H ₂ O		4.27	21.60	-9.20	-7.88	Cal.	Izatt <i>et al.</i> (1976)
H ₂ O, 0.1M HNO ₃		4.21	-	-	-	d.c.Polg.	Luca <i>et al.</i> (1985)
H ₂ O, 0.1M HNO ₃		4.25	-	-	-	a.c.Polg.	Luca <i>et al.</i> (1985)
H ₂ O, 0.1M Et ₄ NClO ₄		3.58	-	-	-	ISE	Brighli <i>et al.</i> (1985)
H ₂ O, 0.5M Li ClO ₄		7.01	-	-	-	Pot.	Kulstad and Malmsten (1981)
H ₂ O, 0.1M Et ₄ NClO ₄		6.90	-	-	-	Pot.	Arnaud <i>et al.</i> (1977)
(50% CH ₃ OH)-H ₂ O		5.12 ± 0.03	30.50 ± 1.95	4.30 ± 0.52	23.80	Cond.	This Work

Table 1. (Continued)

Cation	Solvent	Log K	$-\Delta H^{\circ} / \text{kJ mol}^{-1}$	$-\Delta H^{\circ} / \text{kJ}^{-1} \text{mol}^{-1}$	$\Delta H^{\circ} / T\Delta S^{\circ}$	Method*	Reference
	(70% CH ₃ OH)–H ₂ O	6.50 ± 0.02	37.42 ± 1.82	7.57 ± 0.63	16.59	Cond.	This Work
	(70% CH ₃ OH)–H ₂ O	6.50	38.40	4.60	28.01	Cal.	Izatt <i>et al.</i> (1976)
	(90% CH ₃ OH)–H ₂ O	6.70 ± 0.03	43.10 ± 2.12	16.31 ± 0.84	8.60	Cond.	This Work
	CH ₃ OH	>5	–45	–	–	Cal.	Buschmann (1985)
	CH ₃ OH	>5.5	37.50	–	–	Cal.	Izatt <i>et al.</i> (1986)
	CH ₃ OH, 0.05M Et ₄ NClO ₄	6.99	–	–	–	ISE	Buschmann (1986)
	CH ₃ OH, 0.1M Bu ₄ NClO ₄	7.52	–	–	–	Polg.	Brighli <i>et al.</i> (1985)
	CH ₃ OH, 0.05M Et ₄ NClO ₃	7.70	–	–	–	Pot.	Buschmann (1985)
Cd ²⁺	H ₂ O, 0.1M HNO ₃	2.00	–	–	–	d.c.Polg.	Luca <i>et al.</i> (1985)
	H ₂ O, 0.5M Li HNO ₄	5.59	–	–	–	Pot.	Kulstad (1981)
	H ₂ O, 0.1M Et ₄ NClO ₄	5.31	–	–	–	Pot.	Arnaud <i>et al.</i> (1977)
	CH ₃ OH, 0.05M Et ₄ NClO ₄	7.83	–	–	–	Pot.	Spiess <i>et al.</i> (1980)
	(70% CH ₃ OH)–H ₂ O	2.78 ± 0.02	21.52 ± 1.96	19.4 ± 2.1	3.72	Cond.	This Work
	(90% CH ₃ OH)–H ₂ O	2.90 ± 0.01	26.11 ± 2.13	32.09 ± 1.56	2.73	Cond.	This Work
Cu ²⁺	(90% CH ₃ OH)–H ₂ O	2.65 ± 0.02	17.41 ± 0.93	7.67 ± 0.65	7.62	Cond.	This Work
	CH ₃ OH	2.68	–	–	–	Cond.	Chen <i>et al.</i> (1987)
	CH ₃ OH, 0.1M Bu ₄ NClO ₄	2.47	–	–	–	Polg.	Chen <i>et al.</i> (1987)
Co ²⁺	(90% CH ₃ OH)–H ₂ O	2.45 ± 0.02	15.75 ± 1.02	5.72 ± 0.70	9.23	Cond.	This Work
	CH ₃ OH, 0.01M Bu ₄ NClO ₄	3.41	–	–	–	Polg.	Chen <i>et al.</i> (1987)
Ni ²⁺	(90% CH ₃ OH)–H ₂ O	2.25 ± 0.03	14.35 ± 1.05	4.63 ± 0.62	10.40	Cond.	This Work
	CH ₃ OH	2.51	–	–	–	Cond.	Chen <i>et al.</i> (1987)
	CH ₃ OH, 0.1M Et ₄ Ni	2.47	–	–	–	Polg.	Chen <i>et al.</i> (1987)

* Cond., conductivity; Pot., Potentiometry; Cal., calorimetry; ISE, ion selective electrode; Polg., Polarography.

The reliability of the present $\log K$, ΔH° and ΔS° values determined in aqueous solution for Pb^{2+} and Ag^+ is indicated by the good agreement with those obtained by Izatt *et al.* (1976) using a calorimetric method.

The relative stabilities of the cation complexes of 18-crown-6 in aqueous solution and 90% methanol at 298 K can be examined by calculating the ratio $\Delta H^\circ / T\Delta S^\circ$. The calculated ratio for Pb^{2+} complex in water is considerably smaller and negative than that for Ag^+ complex indicating that the Pb^{2+} complex is entropy stabilized. In case of 90% methanol the Pb^{2+} complex has larger $\Delta H^\circ/T\Delta S^\circ$ ratio (8.60) than the Ag^+ complex (2.76) indicating that the Pb^{2+} complex is more ΔH° favourable than Ag^+ complex (Table 1).

The radii (Shannon 1976, Dalley 1978) of the cations studied and that of 18-crown-6 ring cavity are listed in Table 2. These data, taken with $\log K$ at 298 K in water and in various methanol-water solvents are plotted in Fig. 6 as $\log K$ vs. cationic radius. Fig. 6 shows that $Pb^{2+} - 18C6$ complex has the maximum stability in the series studied. This confirms that the ligand cavity size to cation size is an important factor in determining the stabilities of the complexes formed.

Table 2. Cationic radii and cavity size of 18-crown-6

Cation	Radius, Å	Cation	Radius, Å
Pb^{2+}	1.19	Cu^{2+}	0.73
Ag^+	1.15	Co^{2+}	0.65
Cd^{2+}	0.95	Ni^{2+}	0.63
18-crown-6 (1.34 - 1.43 Å)			

The data in Table 1 show that for the cations Pb^{2+} and Ag^+ , their ionic radii are closer to the lower limit size of 18-crown-6 cavity and are bound more strongly than the cations Cd^{2+} , Cu^{2+} , Co^{2+} and Ni^{2+} which are relatively smaller. This suggests that the $Pb^{2+} - 18C6$ complex has the maximum stability and Pb^{2+} is sit on top of the ligand. The weak complexation of the cations studied which are much smaller than the lower limit size of the ligand is due to their small sizes and probably due to their high heats of solvation. The low values for the stability constants for Ni^{2+} , Cu^{2+} and Co^{2+} complexes are explainable in terms of square planar geometry. Because 18-crown-6 is poorly suited to this geometry, the stability constants are small.

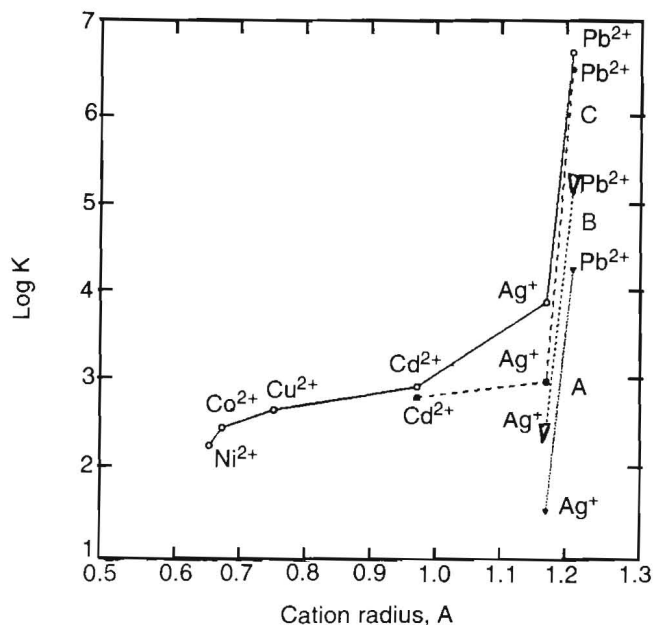


Fig. 6. Plot of Log K vs. cation radius for the 1:1 complexation of 18C6 with Ag^+ , Pb^{2+} , Cd^{2+} , Cu^{2+} , Co^{2+} and Ni^{2+} in 0%-90% methanol- water solvents at 298 K. (A) H_2O ; (B) 50%; (C) 70% and (D) 90%.

The limiting molar conductivities of the 18C6- cation complexes in 90% methanol at 298 K as determined in this work are 65.74, 129.61, 142.24, 149.31, 157.22 and 154.10 $\text{S cm}^2 \text{mol}^{-1}$ for Ag^+ , Pb^{2+} , Cd^{2+} , Co^{2+} and Ni^{2+} , respectively. It has been observed (Takeda *et al.* 1980) that cations having a close fit to a crown ether cavity form the most stable complexes with higher limiting molar conductivities. This observation is in accord with the present results of Pb^{2+} - 18C6 complex.

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دوال الديناميك الحراري لتكوين المعقدات بتفاعل 18-Crown-6 مع أيونات الفلزات Ni^{2+} , Co^{2+} , Cu^{2+} , Cd^{2+} , Pb^{2+} , Ag^{+} في مذيبات ميثانول - ماء بطريقة الموصلية

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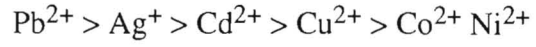
لقد تم في هذا البحث دراسة تكوين المعقدات بتفاعل الايثر التاجي ،
18-crown-6 مع أيونات الفلزات Ni^{2+} , Co^{2+} , Cu^{2+} , Cd^{2+} , Pb^{2+} , Ag^{+} في
مذيبات ميثانول - ماء بواسطة استخدام طريقة الموصلية . وقد تم تعيين قيم
 ΔS° , ΔH° , $\log K$ في مدى من المذيبات يتراوح ما بين 0% إلى 90% ميثانول -
ماء بين درجات الحرارة 288-308 (K) . وقد وجد بأن ثوابت الاستقرار ودوال
الديناميك الحراري تعتمد على طبيعة المذيب وأن هناك علاقة عكسية بين
ثوابت الاستقرار للمعقدات ومانحية جوتمان للمذيبات .

وقد شوهد بأن الموصلية المقاسة ، Λ ، لمعقدات Cd^{2+} , Ag^{+} , Pb^{2+} مع
18-crown-6 تتناقص بشكل ملحوظ عندما تصبح النسبة المولارية ، $[L]_{\circ}$ ،
 $[M^{n+}]_{\circ}$ ، قريبة من الواحد ، بينما للمعقدات Ni^{2+} , Co^{2+} , Cu^{2+} تتناقص Λ
بشكل أقل من ذلك .

في هذا البحث ، تم تحليل الموصلية المولارية المقاسة باستخدام النموذج
١ : ١ القياسي ، وتعيين قيم ثابت الاستقرار ، K ، والموصلية المولارية المحدده ،
 Λ_c ، لكل معقد من الموصلية المولارية المقاسة باستخدام طريقة تحليل المربعات

الأصغر غير الخطية .

وتبين في هذه الدراسة أن متواليّة تكويّن المعقدات في 90% ميثانول-ماء عند درجة الحرارة 298 K وفقاً لقيمة Log K كما يلي :



وقد تم مناقشة أهمية دوال الديناميك الحراري بمعرفة وسط المذيب والحجوم النسبية للايثر التاجي وايونات الفلزات .