

Research Article

Conductometric Studies of Thermodynamics of 1,10-Didecyl-1,10-diaza-18-crown-6 Complexes with Li^+ , Na^+ , K^+ , Cs^+ , NH_4^+ , Mg^{2+} , and Ca^{2+} Ions in Acetonitrile, Methanol, and Ethanol Solutions

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The complexation reactions between 1,10-didecyl-1,10-diaza-18-crown-6 (DD18C6) and Li^+ , Na^+ , K^+ , Cs^+ , NH_4^+ , Mg^{2+} , and Ca^{2+} ions were studied conductometrically in acetonitrile, methanol, and ethanol at various temperatures. The formation constants of the resulting 1 : 1 complexes were calculated from the computer fitting of the molar conductance-mole ratio data at different temperatures. In the solvents studied, the stability of the resulting complexes varied in the order acetonitrile \gg methanol $>$ ethanol. The enthalpy and entropy changes of the complexation reactions were evaluated from the temperature dependence of formation constants. The $T\Delta S^\circ$ versus ΔH° plot of thermodynamic data obtained shows a linear correlation indicating the existence of enthalpy-entropy compensation in the complexation reactions. The ab initio studies calculated at B3LYP/6-31G level of theory indicate that the binding energy of complexes decreases with increasing cation size in the gas phase. The experimental data obtained in the solvents show different trends so that the stability constant of Li^+ and Mg^{2+} complexes is lower than other alkali and alkaline earth ions, respectively due to the solvation of these small ions in solution.

1. Introduction

Since the first discovery of crown ethers by Pedersen [1], the studies of these ligands and their metal ion complexes have become a very popular field of research [2–4], mainly due to their similarities in many respects to the naturally occurring ionophores [5]. Meanwhile, these ligands have demonstrated a high potential for use in many chemical and industrial processes, where cation selectivity and/or solubility in nonpolar solvents are required. Thus, due to the importance of selectivity and stability of the crown ether complexes with different cations in a wide variety of practical applications [6, 7], extensive amount of work in the thermodynamic aspects of the corresponding complexation reactions has also been reported in the literature [8–10].

The stability constants for the 1 : 1 complexes of the alkali and alkaline earth metal ions with 1,10-diaza-18-crown-6 (D18C6) have extensively been determined in various pure solvents [8, 10]. It was of interest to us to study the influence of the cation size (and nature), solvent properties, and bulky substituent in the ligand on the interaction of metal ions with crown ethers.

In this work, we report a conductometric study of the stoichiometry, stability, and thermodynamic parameters of the 1,10-didecyl-1,10-diaza-18-crown-6 (DD18C6) complexes with Li^+ , Na^+ , K^+ , Cs^+ , NH_4^+ , Mg^{2+} , and Ca^{2+} ions in acetonitrile (AN), methanol (MeOH), and ethanol (EtOH) solvents. It should be noted that, while AN, MeOH, and EtOH have about the close dielectric constants (35.94, 32.66, and 24.55, resp.), they possess quite different donor numbers

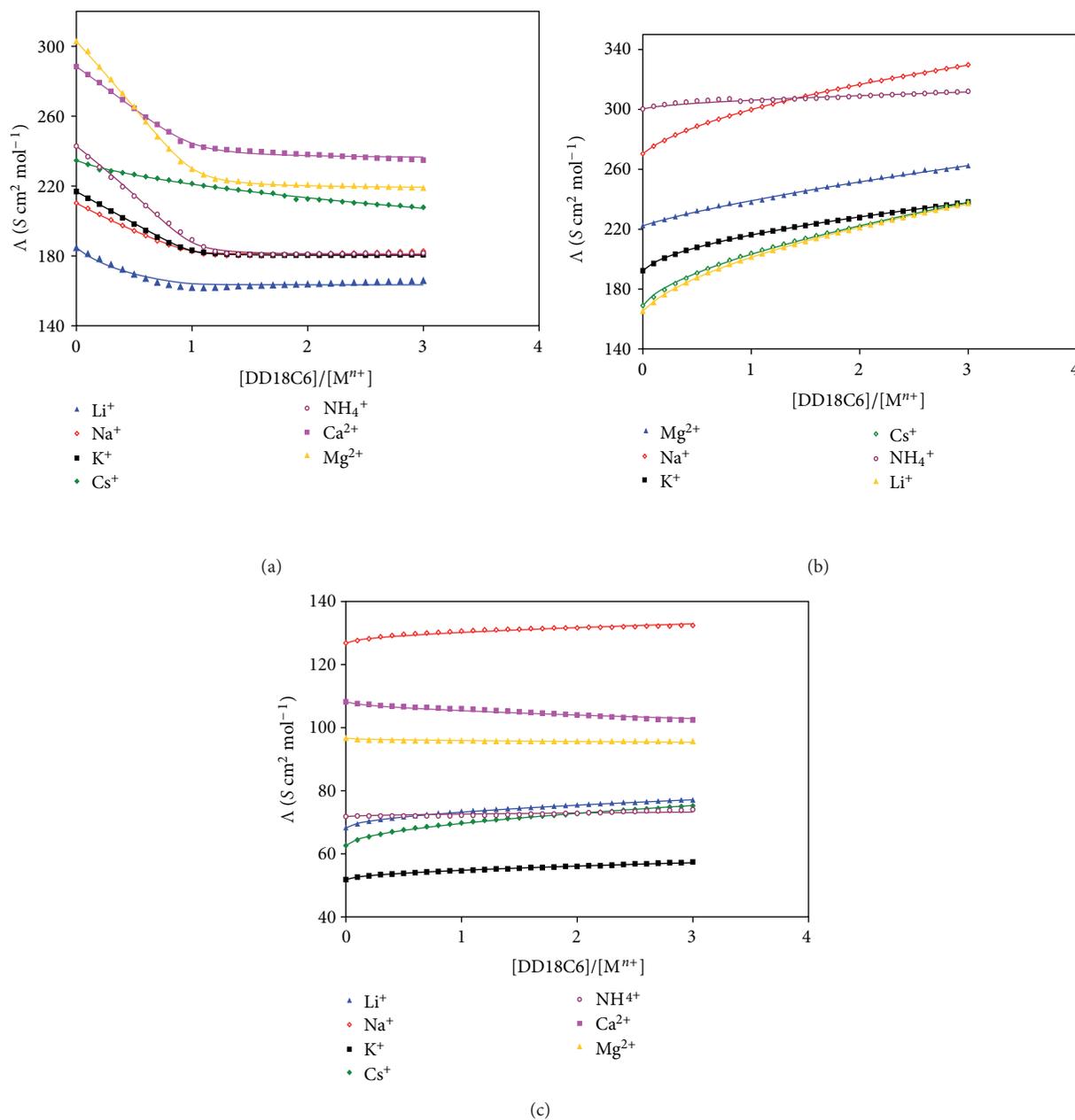


FIGURE 1: Molar conductance ($\text{S cm}^2 \text{ mol}^{-1}$) versus $[\text{DD18C6}]/[\text{M}^{n+}]$ for various DD18C6- M^{n+} systems at 25°C in AN (a), MeOH (b), and EtOH (c). Solid lines represent the fitted curves.

(DN; i.e., DN = 14.1 for AN, DN = 19.0 for MeOH, and DN = 31.5 for EtOH) [11].

2. Experimental

2.1. Reagents. Reagent-grade perchlorate salts of lithium, sodium, potassium, ammonium, and magnesium, nitrate salt of cesium, dried AN ($\text{H}_2\text{O} < 0.005\%$), MeOH, EtOH, and DD18C6 (all from Merck) were of the highest purity available and used as received. $\text{Ca}(\text{ClO}_4)_2$ was prepared by treating CaCO_3 with small excess of 3 M perchloric acid, followed by evaporation to dryness, recrystallization three

times from deionized water, and drying at 120°C. Although we did not encounter any problem, it should be noted that dry perchlorate salts and perchlorate salts in organic solvents are potentially explosive and should be handled only in small quantities with appropriate precautions.

2.2. Conductometric Titration. Conductance measurements were carried out with a Metrohm 712 conductivity meter. A dip-type conductivity cell made of platinum black was used. The cell constant at the different temperatures used was determined by conductivity measurements of a 0.010 M solution of analytical-grade KCl (Merck) in triply distilled

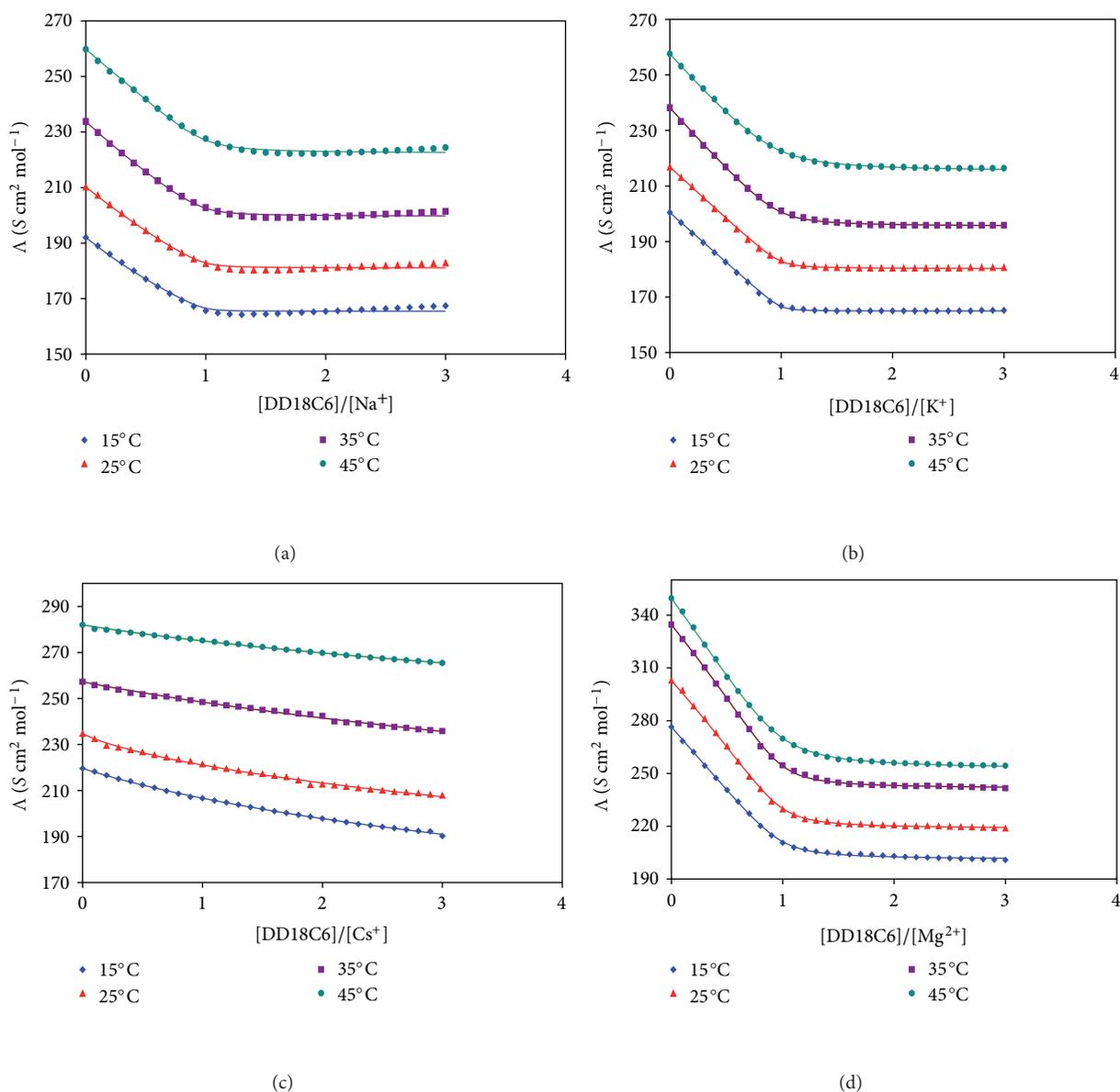


FIGURE 2: Molar conductance ($\text{S cm}^2 \text{ mol}^{-1}$) versus $[\text{DD18C6}]/[\text{M}^{n+}]$ plots in AN at various temperatures. The M^{n+} cations are (a) Na^+ , (b) K^+ , (c) Cs^+ , and (d) Mg^{2+} . Solid lines represent the fitted curves.

deionized water. The specific conductance of this solution at various temperatures has been reported in the literature [12]. In all measurements, the cell was thermostated at the desired temperature $\pm 0.1^\circ\text{C}$ using a Haake D1 thermostat-circulator water bath.

In a typical experiment, 10 mL of the desired metal ion ($5.0 \times 10^{-5} \text{ M}$) was placed in the titration cell, thermostated to the desired temperature, and the conductance of solution was measured. Then, a known amount of a concentrated crown ether solution was added in a stepwise manner using a calibrated micropipette. The conductance of the solution was measured after each addition. The ligand solution was continually added until the desired ligand to cation mole ratio was achieved.

2.3. Calculation of Formation Constant. The formation constants, K_f , and the limiting molar conductances, Λ_o , of the resulting 1 : 1 complexes between DD18C6 and the univalent and divalent cations used, in different solvents and at various temperatures, were calculated by fitting the observed molar conductance, Λ_{obs} , at varying $[\text{DD18C6}]/[\text{M}^{n+}]$ mole ratios to a previously derived equation [13–15] which express the Λ_{obs} as a function of the free and complexed metal ions. A nonlinear least squares curve fitting using Microsoft Excel Solver (version 11.0) was applied for the evaluation of formation constant and limiting molar conductance of the resulting 1 : 1 complexes.

Chi-square statistic was used to evaluate the fitness of equation to the experimental data. The Chi-square test

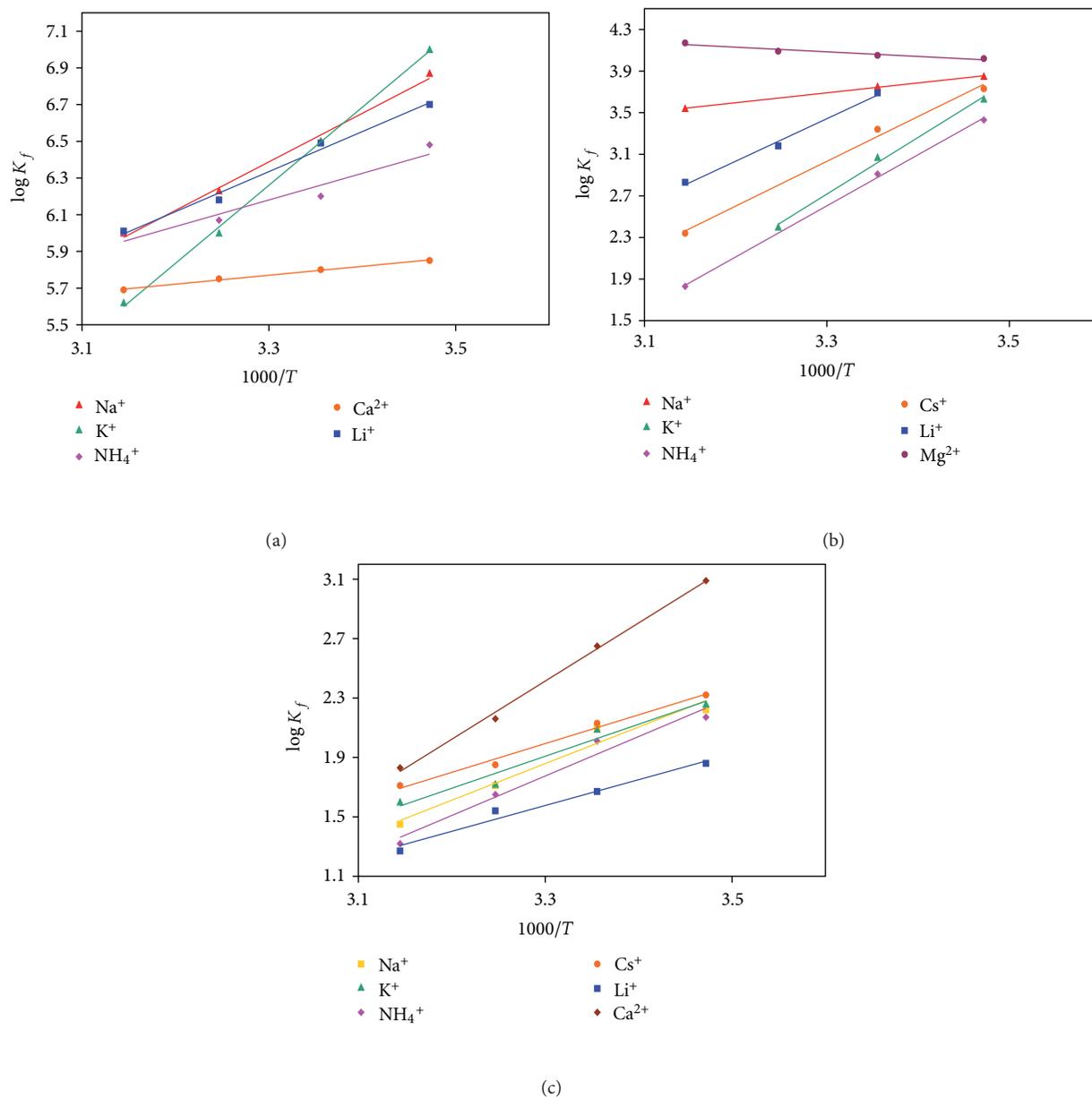


FIGURE 3: Van't Hoff plots for the 1 : 1 complexation of various DD18C6- M^{n+} systems in AN (a), MeOH (b), and EtOH (c).

statistic is the sum of the squares of the differences between the experimental data and data obtained by calculating from (1). The equivalent mathematical statement is:

$$\chi^2 = \sum_{i=1}^N \frac{(\Lambda_{\text{obs.}} - \Lambda_{\text{calc.}})^2}{\Lambda_{\text{calc.}}}, \quad (1)$$

where $\Lambda_{\text{obs.}}$ and $\Lambda_{\text{calc.}}$ are the molar conductance obtained by experimental data and calculating from (2), respectively

$$\Lambda_{\text{cal.}} = \left\{ \left[(K_f C_M - K_f C_L - 1) \right. \right.$$

$$\left. \left. + (K_f^2 C_L^2 + K_f^2 C_M^2 - 2K_f^2 C_L C_M + 2K_f C_L + 2K_f C_M + 1)^{1/2} \right] \frac{(\Lambda_M - \Lambda_{M-L})}{2K_f C_M} \right\} + \Lambda_{M-L}, \quad (2)$$

where K_f is the stability constant of complex, C_L and C_M are the analytical concentrations of DD18C6 and M^+ ion, respectively, and Λ_M and Λ_{M-L} are the respective molar conductance of the free and complexed M^+ ion. If calculated data are similar to the experimental data, χ^2 will be a small number ($\chi^2 < 0.5$); if they are different, χ^2 will be a large number ($\chi^2 > 0.5$).

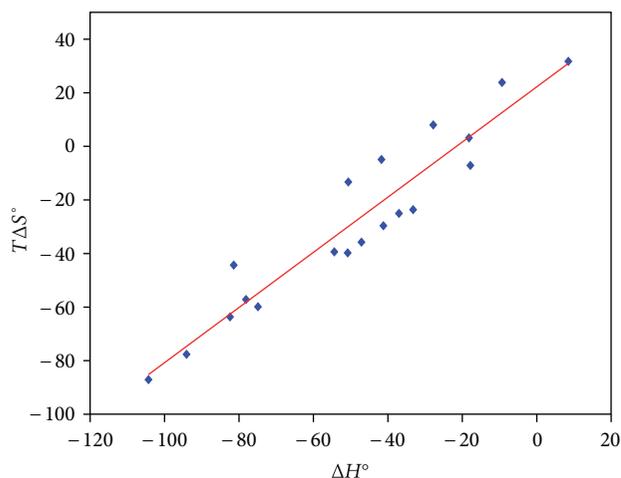


FIGURE 4: Plot of $T\Delta S^\circ$ (kJ mol^{-1}) versus ΔH° (kJ mol^{-1}) for 1 : 1 complexation of Li^+ , Na^+ , K^+ , Cs^+ , Mg^{2+} , Ca^{2+} , and NH_4^+ ions in AN, MeOH, and EtOH solvents ($R = 0.9514$).

2.4. Computational Method. GAMESS R3 2010 Linux code [16] was used for all Density Functional Theory (DFT) calculations. All calculated results belong to the B3LYP/6-31G level of theory. The compilation of the code adopted with Intel's ifort compiler of fortran in conjunction with MKL mathematical library (all are freely accessible from Intel site with non-commercial license). CentOS linux distribution was used as operating system on Intel SMP computer with 16 processors and 32 GB of RAM. All input z-matrixes were prepared with HyperChem program [17], and then Avogadro [18] was used to convert the "pdb" format to "inp" file. The output "log" files were also converted to the "pdb" format to be able to visualize the optimized structures.

3. Results and Discussion

In order to evaluate the influence of adding DD18C6 on the molar conductance of Li^+ , Na^+ , K^+ , Cs^+ , NH_4^+ , Mg^{2+} , and Ca^{2+} ions in AN, MeOH, and EtOH, the molar conductance at a constant salt concentration (5.0×10^{-5} M) was monitored while increasing the crown ether concentration at various temperatures. Some of the resulting molar conductances versus DD18C6/cation mole ratio plots are shown in Figures 1 and 2.

As it is seen, in AN, there is a gradual decrease in the molar conductance with an increase in the crown ether concentration, which begins to level off at a mole ratio greater than one (except Cs^+). Such a conductance behavior is indicative of the formation of fairly stable 1 : 1 complexes in AN.

The formation constants of all DD18C6- M^{n+} complexes in different solvents at various temperatures, obtained by computer fitting of the molar conductance-mole ratio data and Chi square numbers (χ^2), are listed in Table 1. The computer fits of the molar ratio data are shown as solid lines in Figures 1 and 2. The small numbers of Chi square indicate

that our assumption of 1 : 1 stoichiometry seems reasonable in the light of the fair agreement between the observed and calculated molar conductances. It should be noted that, in the procedure of calculation of formation constants, the association between cation and counter ions was considered negligible, under the highly dilute experimental conditions used (5.0×10^{-5} M). Furthermore, since the concentration of crown ether was kept below 1.0×10^{-3} M during the conductometric titrations, the corrections for viscosity changes were also neglected.

In order to have a better understanding of the thermodynamics of complexation reactions of Li^+ , Na^+ , K^+ , Cs^+ , NH_4^+ , Mg^{2+} , and Ca^{2+} ions with DD18C6, it is useful to investigate the enthalpic and entropic contributions to these reactions. The ΔH° and ΔS° of the complexation reactions in different solvents were evaluated from the temperature dependence of the formation constants by applying a linear least-squares analysis according to the Van't Hoff equation. The Van't Hoff plots of $\log K_f$ versus $1/T$ are shown in Figure 3. 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 2.

It is interesting to note that the formation constants obtained in this study at 25°C in AN and MeOH are in satisfactory arrangement with the previously reported values for D18C6 (Table 3).

In the case of complexation of macrocyclic ligands, there are at least three factors which can make significant contributions to the stability of their metal ion complexes: (i) the cation size, (ii) the ionic solvation of the charged species involved, and (iii) conformations of the free and complexed crown ethers. The data given in Table 1 clearly illustrate the fundamental role of the solvent properties in the M^{n+} -DD18C6 complexation reactions studied. In the case of all cations except Cs^+ , the stability of the resulting complexes with DD18C6 varied in the order $\text{AN} \gg \text{MeOH} > \text{EtOH}$. It is well known that the solvating ability of the solvent, as expressed by the Gutmann donor number [11], plays an important role in different complexation reactions [9, 10]. There is actually an inverse relationship between the stabilities of the complexes and the solvating abilities of the solvents. AN has a lower donicity ($\text{DN} = 14.1$) than MeOH ($\text{DN} = 19.0$) and EtOH ($\text{DN} = 31.5$), therefore, shows less competition with the crown ether for mentioned ions; thus, it is not unexpected to observe the highest stability of the complexes in AN and the lowest in EtOH. In the case of DD18C6- Cs^+ , the interaction of the large size central metal ion with solvent is stronger for MeOH than for AN due to higher donicity; therefore, the DD18C6- Cs^+ complex will be stabilized by MeOH solvation and formation constant will be larger.

Table 2 shows that, as expected, for M^{n+} -DD18C6 systems studied, the thermodynamic data vary significantly with the solvent properties. However, the observed increase (or decrease, depending on the nature of the metal ion) in ΔH° value will be compensated by an increase (or decrease) in the corresponding ΔS° value. The existence of such a compensating effect (Figure 4) between ΔH° and ΔS° values has

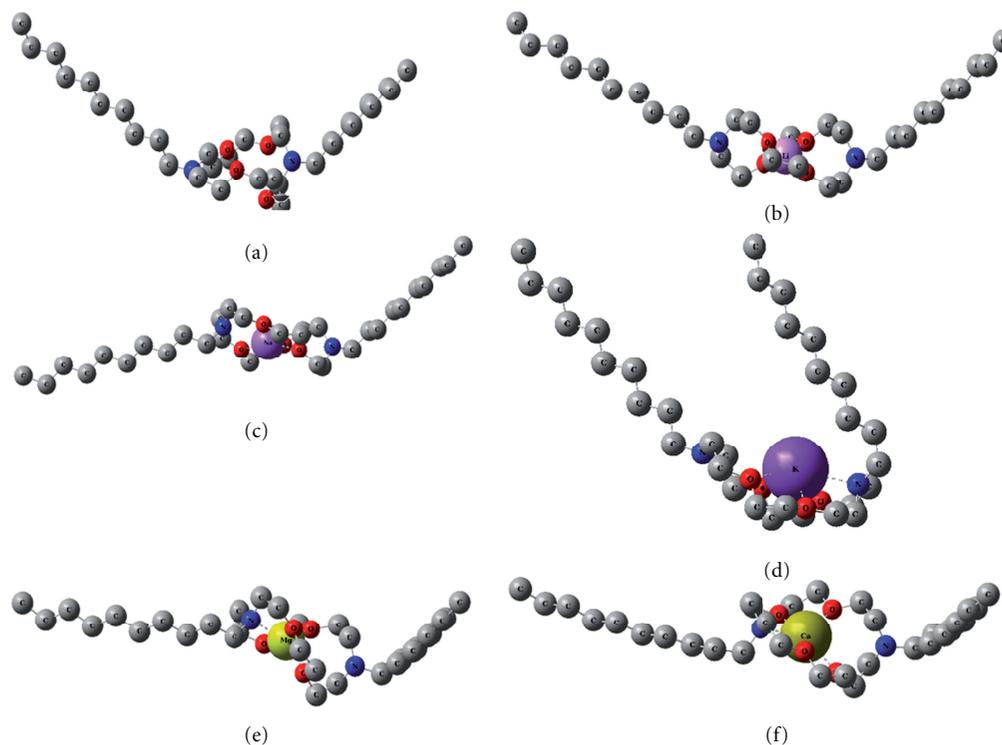


FIGURE 5: The optimized geometries of free DD18C6 (a) and its complexes with Li^+ (b), Na^+ (c), K^+ (d), Mg^{2+} (e), and Ca^{2+} (f). Hydrogen atoms have not been shown for clarity.

TABLE 1: Formation constants for different M^{n+} -DD18C6 complexes in acetonitrile, methanol, and ethanol solvents.

Cation ^a	Solvent	$\text{Log } K_f$							
		15°C	χ^2	25°C	χ^2	35°C	χ^2	45°C	χ^2
Li^+ (0.74)	AN	6.70	0.277	6.49	0.383	6.18	0.117	6.01	0.004
	MeOH	3.04	0.006	3.69	0.009	3.18	0.009	2.83	0.167
	EtOH	1.86	0.141	1.67	0.003	1.54	0.126	1.27	0.027
Na^+ (1.02)	AN	6.87	0.153	6.50	0.104	6.23	0.072	6.00	0.075
	MeOH	3.85	0.006	3.75	0.005	3.58	0.018	3.54	0.021
	EtOH	2.22	0.049	2.10	0.025	1.71	0.009	1.45	0.003
K^+ (1.38)	AN	7.00	0.012	6.50	0.014	6.00	0.011	5.62	0.012
	MeOH	3.63	0.011	3.07	0.007	2.40	0.010	2.28	0.010
	EtOH	2.26	0.012	2.09	0.006	1.72	0.003	1.60	0.004
NH_4^+ (1.48)	AN	6.48	0.016	6.20	0.135	6.07	0.154	6.00	0.004
	MeOH	3.43	0.005	2.91	0.054	2.63	0.068	1.83	0.203
	EtOH	2.17	0.080	2.01	0.062	1.65	0.061	1.32	0.093
Cs^+ (1.70)	AN	2.95	0.008	2.61	0.033	2.31	0.030	1.62	0.007
	MeOH	3.73	0.031	3.34	0.056	3.15	0.024	2.34	0.016
	EtOH	2.32	0.023	2.13	0.010	1.85	0.010	1.71	0.006
Mg^{2+} (0.72)	AN	5.97	0.040	6.04	0.031	6.04	0.031	5.70	0.019
	MeOH	4.02	0.021	4.05	0.047	4.09	0.046	4.17	0.026
	EtOH	1.98	0.017	1.87	0.010	1.77	0.003	1.48	0.013
Ca^{2+} (1.00)	AN	5.85	0.125	5.80	0.097	5.75	0.093	5.69	0.089
	MeOH	4.27	0.059	— ^b	1.02	— ^b	0.86	— ^b	0.64
	EtOH	3.09	0.125	2.65	0.045	2.16	0.105	1.83	0.220

^aThe values in parenthesis are the ionic sizes in Å [15]

^bInsufficient fit.

TABLE 2: Thermodynamic parameters for different M^{n+} -DD18C6 complexes in acetonitrile, methanol, and ethanol solvents.

Cation	Solvent	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔG° (kJ mol ⁻¹)
Li ⁺	AN	-41.7 ± 3.1	-16.5 ± 10.4	-36.8 ± 4.4
	MeOH ^a	-78.1 ± 8.0	-192.0 ± 26.1	-20.9 ± 11.2
	EtOH	-33.2 ± 3.3	-79.4 ± 10.9	-9.5 ± 4.6
Na ⁺	AN	-50.6 ± 3.9	-44.8 ± 13.0	-37.3 ± 5.5
	MeOH ^b	-18.2 ± 0.2	10.5 ± 0.7	-21.4 ± 0.3
	EtOH	-47.1 ± 6.2	-120.1 ± 20.7	-11.4 ± 8.8
K ⁺	AN	-81.4 ± 3.6	-148.9 ± 12.0	-37.1 ± 5.1
	MeOH ^c	-104.3 ± 5.5	-292.2 ± 18.6	-17.2 ± 7.8
	EtOH	-41.2 ± 5.7	-99.6 ± 18.9	-11.6 ± 8.0
NH ₄ ⁺	AN	-27.8 ± 5.9	26.7 ± 19.5	-35.7 ± 8.3
	MeOH ^b	-94.1 ± 0.9	-260.5 ± 2.9	-16.4 ± 1.2
	EtOH	-50.8 ± 5.5	-133.6 ± 18.0	-11.0 ± 7.7
Cs ⁺	AN ^c	-54.4 ± 2.0	-132.3 ± 6.7	-14.9 ± 2.8
	MeOH ^b	-82.4 ± 4.7	-213.8 ± 15.7	-18.7 ± 6.7
	EtOH	-37.0 ± 3.1	-84.0 ± 10.4	-12.0 ± 4.4
Mg ²⁺	AN ^d	— ^d	— ^d	— ^d
	MeOH	8.5 ± 1.4	106.4 ± 4.7	-23.2 ± 2.0
	EtOH ^c	-17.8 ± 0.5	-24.0 ± 1.7	-10.7 ± 0.7
Ca ²⁺	AN	-9.3 ± 0.3	79.9 ± 1.0	-33.1 ± 0.4
	EtOH	-74.9 ± 4.0	-201.1 ± 13.2	-15.0 ± 5.6

^a Without considering Log K_f at 15°C^b Without considering Log K_f at 35°C^c Without considering Log K_f at 45°C^d High uncertainty.TABLE 3: Comparison of stability constants for complexes of 1,10-diaza-18-crown-6 (D18C6) and DD18C6 with Li⁺, Na⁺, K⁺, Cs⁺, Mg²⁺, and Ca²⁺ ions in AN and MeOH solvents at 25°C.

Ligand	Cation	Solvent	Method	Log K_f	Reference	
D18C6	Li ⁺	AN	NMR	4.39	[19]	
DD18C6			Conductometry	6.49	This work	
D18C6	Na ⁺	AN	NMR	4.49	[20]	
DD18C6			Conductometry	4.30	[21]	
D18C6			MeOH	Potentiometry	1.50	[22]
DD18C6	K ⁺	AN	Conductometry	3.75	This work	
D18C6			NMR	4.35	[20]	
DD18C6			Conductometry	4.32	[21]	
D18C6	Cs ⁺	AN	Conductometry	6.50	This work	
DD18C6			MeOH	Potentiometry	1.80	[22]
D18C6			Conductometry	3.07	This work	
DD18C6	Mg ²⁺	MeOH	NMR	2.25	[20]	
D18C6			Conductometry	2.48	[21]	
DD18C6			Conductometry	2.61	This work	
D18C6	Ca ²⁺	MeOH	Potentiometry	3.81	[10]	
DD18C6			Spectrophotometry	3.40	[23]	
D18C6			Conductometry	4.05	This work	
DD18C6	Ca ²⁺	MeOH	Calorimetry	3.87	[24]	
D18C6			Conductometry	4.27 ^a	This work	

^a At 15°C.

TABLE 4: Calculated electronic energies of different species and binding energies of complexes formed by interaction between DD18C6 and Li^+ , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} . All calculations have been done with B3LYP/6-31G.

Compounds	Electronic energy (a.u.)	Binding energy (a.u.)	Binding energy (kcal/mol) ^a
DD18C6	-1668.315091	—	—
Li^+	-7.277405391	—	—
Na^+	-162.0485932	—	—
K^+	-599.6912799	—	—
Mg^{2+}	-199.2015568	—	—
Ca^{2+}	-676.8353899	—	—
DD18C6- Li^+	-1675.786365	-0.193868538	-121.6543491
DD18C6- Na^+	-1830.512579	-0.148894724	-93.43285381
DD18C6- K^+	-2268.111697	-0.105325935	-66.093025
DD18C6- Mg^{2+}	-1868.047261	-0.530613766	-332.965179
DD18C6- Ca^{2+}	-2345.535887	-0.385406425	-241.8461934

^a Binding energy (ΔE) is defined as: $\Delta E = E(\text{complex}) - E(\text{ligand}) - E(\text{ion})$. 1 a.u. is equal to 627.5095 kcal/mol.

been frequently reported for a variety of metal-ligand systems [25, 26]. This effect causes the overall change in the ΔG° value of the complex to be smaller than might be expected from the change in either ΔH° or ΔS° independently.

The formation constants for M^{n+} -DD18C6 and for M^{n+} -D18C6 have been compared in Table 3. The increased formation constant of M^{n+} -DD18C6 as compared to that of M^{n+} -D18C6 must be ascribed to replacement of the solvation layer(s) around cation by the bulky DD18C6 ligand and also to electron donating of the decyl groups, which increase the electron-donor ability of the nitrogen atoms of the ring.

To obtain more information about the structures of complexes, and to investigate that whether ions form complexes in the gas phase or not, the quantum chemical calculations were conducted. The structures were full optimized with no symmetry or any constraints about bond lengths, bond angles, or bond torsions. Five conformations were tested for DD18C6. The conformation with the lowest gas phase energy was chosen for further studies. Figure 5 shows the optimized geometries of both free and complexes of DD18C6 with Li^+ , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} ions. The figure shows that for K^+ -DD18C6 complex, all donor atoms are in one direction, and the ion is placed out of the plane of the cavity, while for Li^+ - and Na^+ -DD18C6, the cavity is twisted, and the ions are placed inside the cavity. The structure of K^+ -DD18C6 is similar to a boat structure, while for Li^+ and Na^+ the structures are similar to a chair. K^+ interact with 5 donor atoms in its boat structure, while Li^+ and Na^+ interact with four oxygen atoms.

Table 4 shows the electronic and binding energies of the species. The data show that there is a strong interaction between each of the studied ions with DD18C6 in the gas phase. From the table, it can be concluded that in the gas phase the binding energy of K^+ with DD18C6 is less than the binding energies of Li^+ and Na^+ with DD18C6. It seems that this less stability (even with 5 interactions) could be related to its boat structure compared to the two other chair structures. Moreover, the surface charge density (charge number/surface area) is smaller for K^+ than Li^+ and Na^+ and hence the interaction of K^+ with crown is weaker. Based

on the ionic radius of Li^+ , Na^+ , and K^+ (Table 1) and the cavity of 18C6 with a radius of 1.3–1.6 Å [15], it is clear that the potassium ion is placed out of the cavity plane. In comparison with the above alkaline ions, Mg^{2+} and Ca^{2+} ions have higher charge density; therefore, it can be concluded that their binding energy in the gas phase should be larger (see the data in Table 4). With enlarging the ionic radius from Mg^{2+} to Ca^{2+} , the crown cavity in the complex form tend to be more planar. Mg^{2+} -DD18C6 has more binding energy than Ca^{2+} -DD18C6.

As it is seen in Table 4, the binding energy decreases monotonically with increasing the size of metal cation. The experimental data in solution (Table 1) shows different trend (Li^+ has the weaker binding energy than Na^+ and K^+ whereas Mg^{2+} has the weaker binding energy than Ca^{2+}). This behavior has also been reported by other researchers [27–30]. The most probable reason for this inconsistency is due to the solvation process of ions. Small ions such as Li^+ and Mg^{2+} have high solvation free energy that causes them to be more solvated in the solution, and have a less interaction with free ligand.

4. Conclusion

From the conductometric results obtained on the thermodynamics of complexation of DD18C6 with some alkali and alkaline earth metal ions in acetonitrile, methanol, and ethanol solvents and quantum chemical calculations, it can be concluded the following.

- (1) The solvents illustrate the fundamental role in the M^{n+} -DD18C6 complexation reactions. The stability of the resulting complexes (except Cs^+) varied in the order acetonitrile \gg methanol $>$ ethanol.
- (2) Although the enthalpy and entropy changes are strongly solvent dependent, the observed increase (or decrease) in ΔH° value will be compensated by an increase (or decrease) in the corresponding ΔS° value.

- (3) The quantum chemical calculations in the gas phase indicate that the binding energy of complexes decreases with increasing cation size.

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