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Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

SPECTROPHOTOMETRIC STUDY OF THE THERMODYNAMICS OF COMPLEXATION OF LITHIUM AND SODIUM IONS WITH DIBENZO-24-CROWN-8 IN BINARY DIMETHYLFORMAMIDE-ACETONITRILE MIXTURES USING MUREXIDE AS A METALLOCHROMIC INDICATOR

Habibollah Khajesharifi^a; Mojtaba Shamsipur^a

^a Department of Chemistry, Shiraz University, Shiraz, Iran

To cite this Article Khajesharifi, Habibollah and Shamsipur, Mojtaba(1995) 'SPECTROPHOTOMETRIC STUDY OF THE THERMODYNAMICS OF COMPLEXATION OF LITHIUM AND SODIUM IONS WITH DIBENZO-24-CROWN-8 IN BINARY DIMETHYLFORMAMIDE-ACETONITRILE MIXTURES USING MUREXIDE AS A METALLOCHROMIC INDICATOR', *Journal of Coordination Chemistry*, 35: 3, 289 – 297

To link to this Article: DOI: 10.1080/00958979508024040

URL: <http://dx.doi.org/10.1080/00958979508024040>

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SPECTROPHOTOMETRIC STUDY OF THE THERMODYNAMICS OF COMPLEXATION OF LITHIUM AND SODIUM IONS WITH DIBENZO-24-CROWN-8 IN BINARY DIMETHYLFORMAMIDE-ACETONITRILE MIXTURES USING MUREXIDE AS A METALLOCHROMIC INDICATOR

HABIBOLLAH KHAJESHARIFI and MOJTABA SHAMSIPUR*

Department of Chemistry, Shiraz University, Shiraz, Iran

(Received August 3, 1994; in final form November 10, 1994)

Complexation of Li^+ and Na^+ with dibenzo-24-crown-8 has been studied in dimethylformamide-acetonitrile mixtures by means of a competitive spectrophotometric technique using murexide as metal ion indicator. Stabilities of the resulting 1:1 complexes were investigated at various temperatures and enthalpies and entropies of complexation were determined from the temperature dependence of the formation constants. Sodium forms a more stable complex with the crown ether than lithium. There is an inverse linear relationship between $\log K_f$ and the mole fraction of DMF in the solvent mixtures. The $\Delta H^\circ - T\Delta S^\circ$ plot of all thermodynamic data, obtained for both crown complexes in different solvent mixtures, shows a fairly good linear correlation, indicating the existence of an enthalpy-entropy compensation effect in complexation.

KEYWORDS: Li^+ , Na^+ , DB24C8, murexide, DMF-AN mixture, stability constants, thermodynamics, spectrophotometry

INTRODUCTION

Since the first synthesis of macrocyclic polyethers (crown ethers),¹ studies of these ligands and their metal ion complexes have received increasing attention.²⁻⁴ By variation of ring parameters and structural units such as ring size, number and type of donor atoms and nature of substituents, macrocyclic ligands which can selectively bind cations, anions and even molecular compounds^{4,5} have been prepared.

Studies of larger crown ethers such as dibenzo-30-crown-10 and dibenzo-24-crown-8 have shown that these molecules and their alkali and alkaline earth metal complexes may possess a variety of conformations.⁶⁻¹⁰ In addition, complexes of different crown to metal ion ratios may be isolated in crystalline form and observed

*Author for correspondence.

in solution.^{6,10-12} Due to the three-dimensional 'wrap around' structures of some large crown ether-metal ion complexes, they may be used as proper synthetic models for naturally occurring cyclic antibiotic ionophores.¹³

It was of interest to us to study the thermodynamics^{10,14-18} and kinetics^{19,20} of the complexation of large crown ethers with alkali and alkaline earth cations in non-aqueous and mixed solvents. In this paper we report a thermodynamic study of the complexation of Li⁺ and Na⁺ ions with dibenzo-24-crown-8 in dimethylformamide-acetonitrile mixtures.

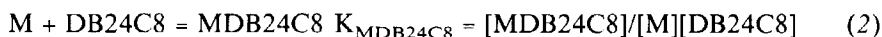
EXPERIMENTAL

All chemicals used were purchased from Merck chemical company. Perchlorate salts of lithium and sodium and murexide were of the highest purity available and were used without further purification except for vacuum drying over P₂O₅. The ligand, 1, 13-dibenzo-24-crown-8 (DB24C8) was recrystallized from reagent grade *n*-heptane and vacuum dried. Spectroscopic grade dimethylformamide (DMF) and acetonitrile (AN) were used as received.

All spectra were recorded on a Philips PUB750 ratio recording spectrophotometer and absorbance measurements were made with a Metrohm 662 photometer at 15.0, 25.0, 35.0 and 45.0 °C. At all temperatures, the cell was thermostatted with a Lo-Temprol 154 thermostat to ±0.1 °C.

Formation constants of 1:1 complexes between Li⁺ and Na⁺ ions and murexide (Mu, as coloured ligand) and DB24C8 (as buffer ligand) in different DMF-AN solvent mixtures were determined by absorbance measurements at λ_{max} of the metal ion-murexide complex, of solutions in which constant concentrations of both ligands (1.0 × 10⁻⁵ – 5.0 × 10⁻⁵ M of murexide and 0.004–0.010 M of DB24C8) were titrated with a concentrated metal ion solution in the same solvent mixture (0.100 M) using a pre-calibrated microlitre syringe. Attainment of equilibrium was checked by observation of no further change in spectra after several hours.

When an alkali cation reacts with murexide and DB24C8 to form 1:1 complexes, the corresponding formation constants are given as



(charges are omitted for simplicity). Mass balance equations and the observed absorbance, A_{obs}, are given as

$$C_{Mu} = [Mu] + [MMu] \quad (3)$$

$$C_{DB24C8} = [DB24C8] + [MDB24C8] \quad (4)$$

$$C_M = [M] + [MMu] + [MDB24C8] \quad (5)$$

$$A_{obs} = \epsilon_{Mu}[Mu] + \epsilon_{MMu}[MMu] \quad (6)$$

where C and ε values are the analytical concentration and molar absorptivity of the species indicated, respectively. The mass balance equations can be solved in order to obtain an equation for the free metal ion concentration, [M], as follows.

$$K_{MMu} K_{MDB24C8} [M]^3 \{K_{MMu} K_{MDB24C8} (C_M - C_{Mu} - C_{DB24C8}) - K_{MMu} - K_{MDB24C8}\} \\ [M]^2 - \{K_{MDB24C8} (C_M - C_{DB24C8}) + K_{MMu} (C_{Mu} - C_M) - 1\} [M] - C_M = 0 \quad (7)$$

For evaluation of the formation constants from the absorbance vs C_M/C_{Mu} mole ratio data, a non-linear, least-squares curve fitting program, KINFIT, was used.²¹ The program is based on the iterative adjustment of calculated values of absorbance to observed values by using either the Wentworth matrix technique²² or the Powell procedure.²³ Adjustable parameters are the formation constants K_{MMu} and $K_{MDB24C8}$ and molar absorptivities ϵ_{Mu} and ϵ_{MMu} .

The free metal ion concentration was calculated from equation (7) by mean of a Newton-Ralphson procedure. Once the value of $[M]$ had been obtained, the concentrations of all other species involved were calculated from the mass balance equations (3) to (5) using the estimated values of the formation constants and molar absorptivities of the current iteration step of the program. Refinement of the parameters was continued until the sum-of-squares of the residuals between calculated and observed values of absorbance for all experimental points was minimized. The output of the program KINFIT comprises refined parameters, the sum-of-squares and the standard deviation of data.

RESULTS AND DISCUSSION

The visible spectra of murexide and its lithium and sodium complexes in 10% (w/w) DMF-AN mixture are shown in Figure 1. The spectroscopic behavior of the murexide complexes is quite unique in all binary mixtures used, consisting of strong shifts (30-50 nm) toward shorter wavelengths, in comparison to free murexide. Reasons for such strong and ion-specific blue shifts are discussed elsewhere.²⁴⁻²⁶ It is well known that murexide forms a 1:1 complex with alkali and alkaline earth cations in nonaqueous media.^{25,26} Formation of such 1:1 complexes between murexide and Li^+ and Na^+ ions in different DMF-AN mixtures was further confirmed by observing a well-defined isosbestic point in the corresponding murexide spectra during the titration with metal ions and also by excellent computer fitting of the resulting absorbance-mole ratio data (Figure 2A) to the 1:1 metal ion-murexide stoichiometry.

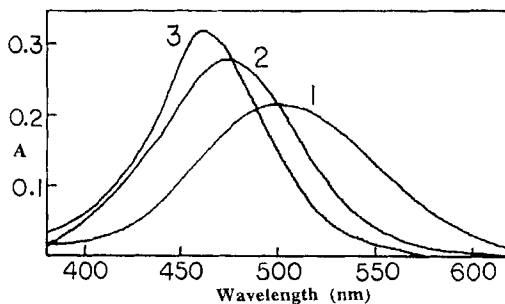


Figure 1 Visible spectra of murexide (1) and its complexes with Na^+ (2) and Li^+ (3) ions in 10% DMF-AN.

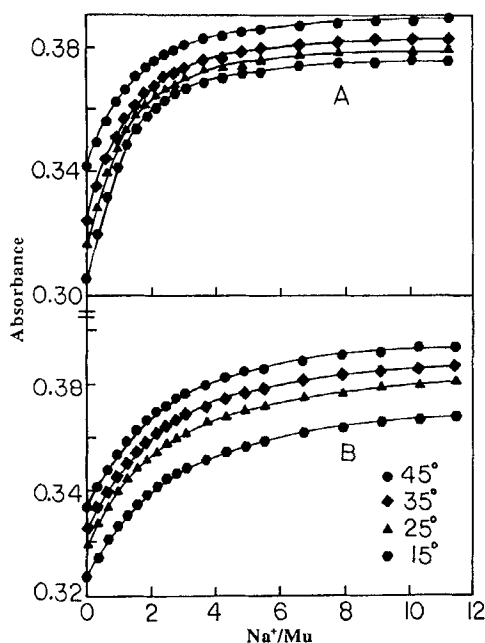


Figure 2 Absorbance-mole ratio plots for the Na^+ -murexide system in the absence (A) and presence (B) of DB24C8 in 30% DMF-AN at various temperatures.

The formation constants of Li^+ and Na^+ ions with murexide and DB24C8 in different DMF-AN solvent mixtures were obtained at various temperatures by absorbance measurements, at λ_{max} of the murexide complexes, of solutions in which varying concentrations of metal ions were added to fixed amounts of murexide and DB24C8 in the solvent mixtures. Sample absorbance-mole ratio plots are shown in Figure 2. All the resulting formation constants, evaluated from computer fitting of the absorbance-mole ratio data, are summarized in Table 1. A sample computer fit of the data is shown in Figure 3. Our assumption of 1:1 stoichiometry for the murexide and DB24C8 complexes with Li^+ and Na^+ ions seems reasonable in the light of the agreement between the observed and calculated absorbances.

It is interesting to note that, in the absorbance-mole ratio plots shown in Figure 2, the absorbances of the starting points and those of the saturated regions vary with temperature (as a result of changes in ϵ values). Thus, the possibility of thermochromism in the alkali ion-murexide systems, under the experimental conditions used, cannot be ignored.

In order to better understand the thermodynamics of complexation, it is useful to consider the enthalpic and entropic contributions to the reactions. Thermodynamic parameters were calculated from the temperature dependence of the complex formation constants. Plots of $\log K_f$ vs $1/T$ in all cases were linear (see for example Figure 4) and ΔH° and ΔS° values were determined in the usual manner from the slope and intercept of the plots, respectively. The results are also included in Table 1.

Table 1 Formation Constants ($\log K_f$ in M^{-1}) and Thermodynamic Parameters (ΔH° in kJ/mol ; ΔS° in $J/mol K$) for the Reaction of Li^+ and Na^+ Ions with Murexide and DB24C8 in DMF-AN Mixtures.

Ligand	X_{DMF}^a	Ion	Log K_f				$-\Delta H^\circ$	ΔS°
			15°C	25°C	35°C	45°C		
Murexide	0.06	Li^+	5.38 ± 0.02	5.34 ± 0.04	5.32 ± 0.01	5.29 ± 0.02	5.0 ± 0.3	86 ± 2
		Na^+	5.03 ± 0.02	4.97 ± 0.04	4.93 ± 0.02	4.90 ± 0.01	7.6 ± 0.5	71 ± 2
	0.12	Li^+	5.33 ± 0.04	5.28 ± 0.04	5.26 ± 0.05	5.22 ± 0.04	6.0 ± 0.7	82 ± 3
		Na^+	5.01 ± 0.01	4.95 ± 0.03	4.90 ± 0.03	4.88 ± 0.04	7.8 ± 0.7	70 ± 3
	0.19	Li^+	5.26 ± 0.03	5.21 ± 0.01	5.18 ± 0.03	5.15 ± 0.04	6.3 ± 0.4	79 ± 2
		Na^+	4.99 ± 0.02	4.93 ± 0.04	4.89 ± 0.01	4.87 ± 0.02	7.0 ± 0.7	72 ± 2
	0.27	Li^+	5.21 ± 0.02	5.14 ± 0.03	5.10 ± 0.01	5.05 ± 0.02	9.0 ± 0.4	69 ± 2
		Na^+	4.96 ± 0.01	4.90 ± 0.01	4.87 ± 0.04	4.85 ± 0.03	6.4 ± 0.7	73 ± 3
DB24C8	0.06	Li^+	3.41 ± 0.08	3.29 ± 0.04	3.12 ± 0.07	3.02 ± 0.03	23 ± 1	14 ± 4
		Na^+	3.58 ± 0.02	3.52 ± 0.04	3.54 ± 0.07	3.40 ± 0.03	10.7 ± 0.3	33 ± 2
	0.12	Li^+	3.40 ± 0.08	3.22 ± 0.07	3.04 ± 0.05	2.95 ± 0.04	25 ± 1	-20 ± 5
		Na^+	3.55 ± 0.08	3.47 ± 0.08	3.37 ± 0.05	3.32 ± 0.02	13.9 ± 0.7	21 ± 3
	0.19	Li^+	3.33 ± 0.07	3.14 ± 0.02	2.98 ± 0.07	2.80 ± 0.07	27 ± 1	-27 ± 4
		Na^+	3.53 ± 0.07	3.41 ± 0.04	3.30 ± 0.02	3.25 ± 0.02	17 ± 1	10 ± 3
	0.27	Li^+	3.28 ± 0.02	3.05 ± 0.04	2.90 ± 0.08	2.80 ± 0.07	28 ± 2	-31 ± 7
		Na^+	3.49 ± 0.04	3.34 ± 0.06	3.27 ± 0.03	3.13 ± 0.02	21.0 ± 0.8	-6 ± 1

^aThese solutions have the following wt% DMF:0.06(10%); 0.12(20%); 0.19(30%); 0.27(40%).

From the data given in Table 1, it is obvious that the stability of the resulting complexes is strongly dependent on the solvent mixture composition. In all cases, stability decreases with increasing fraction of DMF. It should be noted that, while DMF and AN possess about the same dielectric constants (38.0 for DMF and 36.1 for AN), their solvating abilities are quite different.²⁷ DMF is a solvent of higher Gutmann donor number ($DN = 26.6$) than AN ($DN = 14.1$) so that it can strongly compete with other ligands for metal ions. Thus it is not surprising to observe a decrease in stability of the complexes with increasing amounts of DMF in the solvent mixtures. It is interesting to note that there is actually a linear relationship between $\log K_f$ of the complexes and the mole fraction of DMF (Figure 5). We have frequently observed similar behaviour for different metal ion-ligand systems in various mixed solvents.^{15,28-33} Such monotonic behaviour can be related to the preferential solvation of the cations by DMF molecules.

Thermodynamic data for lithium and sodium complexes with murexide are given in Table 1. To the best of our knowledge, there is no reported ΔH° and ΔS° value for the above complexes in the literature. The only reported values are for murexide complexes with cobalt, nickel and copper ions in aqueous solution³⁴ and in alcohol-water mixtures.^{28,35} However, the data obtained in this study show a similar trend with those reported for the murexide-transition metal complexes;^{28,34,35} the thermodynamic data vary with solvent composition, and ΔH° and ΔS° values show that the complexes are stabilized by both the enthalpy and entropy terms. The sign and magnitude of the ΔS° values are consistent with 'chelate effect'.³⁶

As the data given in Table 1 show, in all solvent mixtures used, Na^+ forms a more stable 1:1 complex than Li^+ with DB24C8. Although the isolation of a 2:1 adduct (metal to ligand) between sodium and DB24C8 in crystalline form has been reported previously,³⁷ there is no evidence for the formation of such 2:1 complex in non-aqueous solutions.^{14,18,38-41} It should be noted that the role of the counter

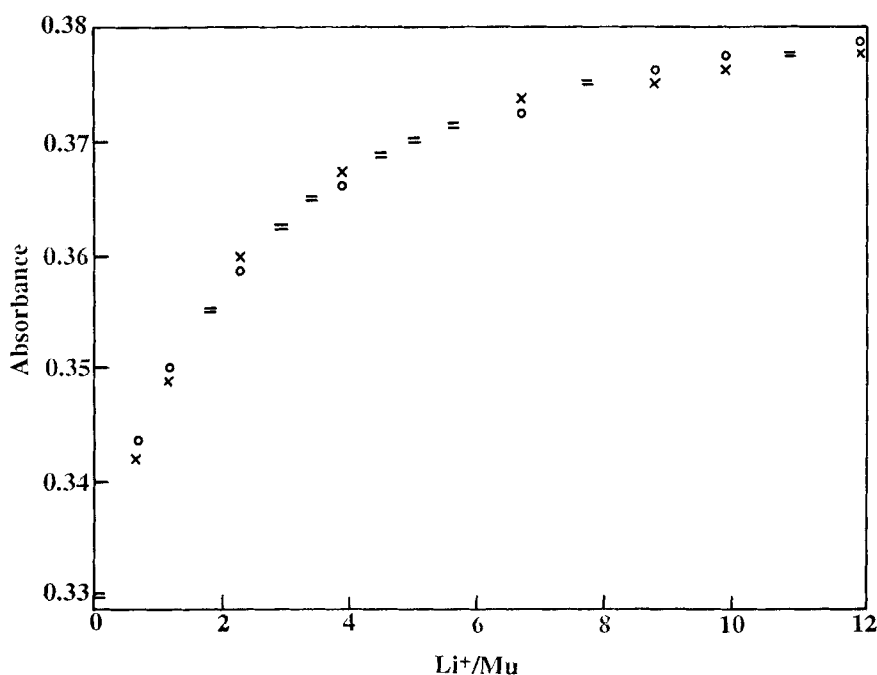


Figure 3 Computer fit of absorbance vs Li^+/Mu mole ratio plot in the presence of DB24C8 in 30% DMF-AN mixture at 35 °C: (x) experimental point; (o) calculated point; (=) experimental and calculated points are the same within the resolution of the plot.

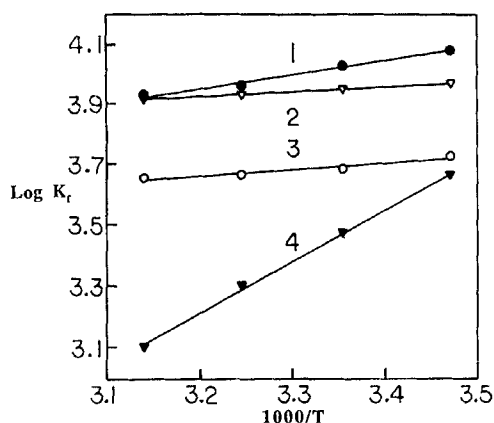


Figure 4 Van't Hoff plots for the Na^+ -DB24C8 system in different DMF-AN mixtures. Weight percent DMF in the solvent mixture is 1, 10%; 2, 20%; 3, 30%; 4, 40%.

anion in the formation of the 2:1 complex is of great importance. The crystallographic structure of the 2:1 sodium *o*-nitrophenolate complex with DB24C8³⁷ shows the partition of the ligand molecule in two distinct and symmetrical regions

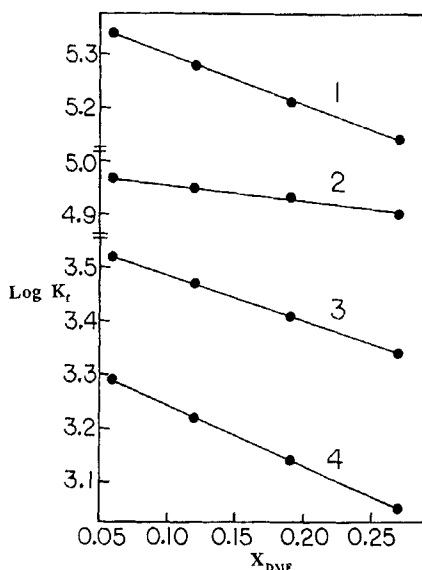


Figure 5 Variation of stabilities of different murexide and DB24C8 complexes with X_{DMF} : 1, $Li^+ Mu$; 2, $Na^+ Mu$; 3, $Na^+ DB24C8$; 4, $Li^+ DB24C8$.

in which each sodium ion is hexacoordinated to the bidentate anion and four ether oxygens of the ring.

It is interesting to note that extrapolation of the linear plot of $\log K_f$ vs X_{DMF} (Figure 5) to a DMF mole fraction of zero results in $\log K_f = 4.16$ for $Na^+ - DB24C8$ in pure acetonitrile, a value which is in satisfactory agreement with the previously reported $\log K_f = 4.00$ in this solvent.³⁸ Unfortunately, there is no reported formation constant for $Li^+ - DB24C8$ complex in the literature for comparison.

For large crown ethers, which are capable of forming three-dimensional 'wrap around' complexes with smaller cations,^{6,9,10,14-18} it can be expected that the cation will strongly influence complex formation. Complexation of a large crown ether by a cation of proper size results in the formation of a stable 'wrap around' complex. If the cation is too large, this three-dimensional structure cannot be formed and only some of the donating oxygen atoms can bond to the cation; consequently a weaker complex results. On the other hand, if the ring size is much larger than the cation, the ligand can still form such a three-dimensional structure, but in this case the oxygen atoms of the ligand have to be in a close proximity and the resulting repulsive forces will weaken the complex. The relatively large variation of the stability of Li^+ and Na^+ complexes of DB24C8 with DMF mole fraction (Figure 5) indicates that the cationic charge is not effectively shielded by the DB24C8 cavity, and that the central cation remains more or less exposed to the solvent molecules.

Thermodynamic data (Table 1) show that, in all solvent mixtures used, both Li^+ and Na^+ complexes with DB24C8 are enthalpy stabilized. On the other hand, while the $Li^+ DB24C8$ complex is entropy destabilized, in all DMF-AN mixtures, $Na^+ DB24C8$ is entropy stabilized (except in 40% DMF-AN mixture). As is seen, the enthalpy and entropy values vary significantly with solvent composition. It has been reasonably assumed that the decrease in entropy upon complexation is related

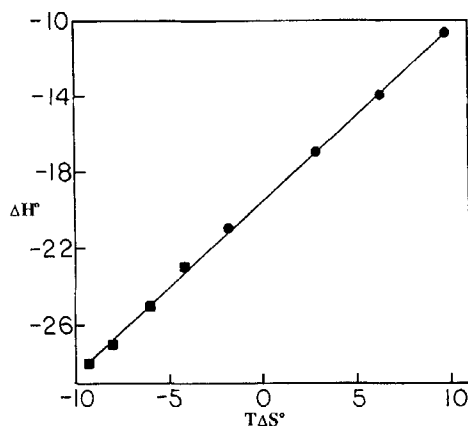


Figure 6 Plot of ΔH° vs $T\Delta S^\circ$ for 1:1 complexation of Li^+ and Na^+ with DB24C8 in different DMF-AN mixtures: (●) Na^+ DB24C8; (■) Li^+ DB24C8.

to a change in conformational entropy of the ligand.^{10,14} Large macrocyclic ligands such as DB24C8 should be rather flexible in the free state, and the degree of flexibility would vary with the size of the ligand as well as with the ligand-solvent interaction. Complex formation between a macrocyclic ligand and a metal ion results in diminished flexibility of the ligand; the more rigid the complex, the more negative the conformational entropy of the system. Thus, the resulting negative ΔS° for Li^+ DB24C8 seems to reflect its higher rigidity compared to Na^+ DB24C8.

As can be seen from Table 1, for the case of both Li^+ and Na^+ complexes with DB24C8, the ΔS° values shift to more negative values with decreasing amounts of AN in the mixed solvent, most probably due to decreased ligand-solvent interaction. It is well known that in AN solution there are rather strong interactions between crown ethers and solvent molecules.^{42,43} Simultaneously, ΔH° shifts to more negative values. Consequently, the negative change in entropy may cancel some of the enthalpic gain due to stronger bonding. Thus, it is obvious that, in all cases, ΔH° and ΔS° compensate each other with ΔH° being the dominant factor responsible for the stability of the resulting Li^+ and Na^+ complexes.

As shown in Figure 6, there is a fairly good linear relationship between ΔH° and $T\Delta S^\circ$ values. The regression equation for the ΔH° vs $T\Delta S^\circ$ plot is in the form

$$\Delta H^\circ = \Delta H^\circ_0 + \alpha T\Delta S^\circ \quad (8)$$

with $\Delta H^\circ_0 = 19.5$ kJ/mol, $\alpha = 0.90$ and the regression coefficient $r = 0.9996$. Equation (8) shows that the enthalpic change consists of two components, one of which is independent of ΔS° and the other proportional to it. Moreover, this equation shows that the complex stability is of enthalpic origin. The α value can be considered as a quantitative measure of the entropic compensating effect. For a value of $\alpha = 0.90$, only 10% of the change in $T\Delta S^\circ$ contributes to the change in complex stability.

The negative intercept means that complex formation can occur even in the absence of any entropic change. Negative ΔS° results in stronger cation-ligand binding. This can happen in cases where the dominant factor in determining the

ΔS° of complexation is the conformational change of DB24C8 from a rather flexible structure in the free state to a rigid structure in the complexed form. In such a case, the positive change in entropy due to the desolvation of the cation should be negligible. Positive ΔS° , on the other hand, results in weaker cation-ligand binding; solvation of the cation competes with the cation-ligand interaction.

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