

Thermodynamic study for dicyclohexano-24-crown-8 complexes with K^+ , Rb^+ , Cs^+ and Tl^+ ions in binary acetonitrile–nitromethane mixtures by conductometric method

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Abstract The complexation reactions between dicyclohexano-24-crown-8 (DC24C8) and K^+ , Rb^+ , Cs^+ and Tl^+ ions were studied conductometrically in the different acetonitrile–nitromethane mixtures 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. At 25 °C and in all solvent mixtures used, the stability of the resulting complexes varied in order of $Tl^+ > K^+ > Rb^+ \sim Cs^+$. The enthalpy and entropy changes of the complexation reactions were evaluated by the temperature dependence of formation constants. It was found that the stability of the resulting complexes increased with increasing nitromethane in the solvent mixture.

Keywords Dicyclohexano-24-crown-8 · K^+ , Rb^+ , Cs^+ and Tl^+ complexes · Conductance · Stability · Mixed solvent

Introduction

Since the first discovery of crown ethers was done by Pedersen [1], the studies of these ligands and their metal

ion complexes have become a very popular field of research [2–5], mainly due to their similarities in many respects to the naturally occurring ionophores [6, 7]. 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, owing to the importance of selectivity and stability of the crown ether complexes with different cations in a wide variety of practical applications [8–10], extensive amount of work in the thermodynamic aspects of the corresponding complexation reactions has also been reported in the literature [11–13]. While crown ether complexes of alkali and alkaline earth cations in aqueous and neat nonaqueous solvents have been extensively reported in the literature, the complexation reaction of these complexes in mixed solvent systems have been investigated only to a very limited extent.

Among the macrocyclic polyethers, large crown ethers (i.e., larger than 18-crown-6) possess interesting complexation properties. Some of these ligands are very flexible molecules with enough oxygen atoms in their rings to enable them to twist around a metal ion of suitable size to envelop it completely and form a “wrap around” complex in which all oxygen atoms of the ring are coordinated to the central cation. Evidence for the formation such three-dimensional structures both in solid state [14, 15] and in solution [16–19] has been reported. Moreover, in some cases, the large macrocyclic ring can accommodate two cations, if the repulsion forces are not so large, as in the case of Li^+ , Na^+ and K^+ complexes with dibenzo-24-crown-8 [20, 21] and dibenzo-30-crown-10 [16, 22].

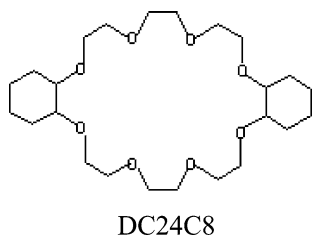
With the aim of studying the influence of the cation size (and nature) and solvent properties on the interaction of metal ions with large crown ethers, we report a conductometric study of the stoichiometry, stability and

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thermodynamic parameters of the dicyclohexano-24-crown-8 (DC24C8) complexes with K^+ , Rb^+ , Cs^+ and Tl^+ ions in binary acetonitrile (AN)–nitromethane (NM) mixtures. It should be noted that, while AN and NM have about the same dielectric constants, they possess quite different donor numbers, DN (i.e., DN = 14.1 for AN and DN = 2.7 for NM) [23].



Experimental

Reagent-grade potassium perchlorate, dried acetonitrile ($H_2O < 0.005\%$) from Merck and DC24C8 from Aldrich were of the highest purity available and used as received. $TlClO_4$, $RbClO_4$ and $CsClO_4$ were prepared by treating $TlNO_3$, $RbCl$ and $CsNO_3$, respectively, with small excess of 3 M perchloric acid, evaporation to dryness, recrystallization three times from deionized water and drying at 120 °C. Reagent-grade nitromethane (Merck) was dried over magnesium sulfate and then distilled three times. The conductivity of the product was less than 5.0×10^{-7} S cm^{-1} at 25 °C. All the AN–NM mixtures used were prepared by weight.

Conductance measurements were carried out with a CMD 500 WPA 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 thrice distilled deionized water. The specific conductance of this solution at various temperatures has been reported in the literature [24]. In all measurements, the cell was thermostated at the desired temperature ± 0.03 °C using an EDMUND BUHLER model KT4 thermostat-circulator water bath.

In a typical experiment, 10 mL of the desired metal ion (5.0×10^{-5} 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.

The formation constants, K_f , and the limiting molar conductances, Λ_o , of the resulting 1:1 complexes between DC24C8 and the mentioned univalent cations, were calculated in different AN–NM mixtures at various temperatures. These calculations were done by fitting the observed molar conductance, Λ_{obs} , at varying $[DC24C8]/[M^+]$ mole ratios to the equation which express Λ_{obs} as a function of the free and complexed metal ions [25, 26]. Moreover, the formation constants were evaluated using a non-linear least-squares curve-fitting program KINFIT [27]. The details are described elsewhere [28].

Results and discussion

In order to evaluate the influence of adding DC24C8 on the molar conductance of K^+ , Rb^+ , Cs^+ and Tl^+ ions in different AN–NM mixtures, 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 $[DC24C8]/[cation]$ mole ratio plots are shown in Figs. 1 and 2.

As shown in Figs. 1 and 2, in all cases, there is a gradual decrease in the molar conductance with an increase in the crown ether concentration. This behavior indicates the lower mobility of the complexed cations compared to the solvated ones. Figure 1 shows that, in the case of Tl^+ –DC24C8 system and in all binary AN–NM mixtures studied, the addition of DC24C8 to the Tl^+ ion solution causes a continuous decrease in the molar conductance, which begins to level off at a mole ratio greater than one. Such conductance behavior is indicative of the formation of fairly stable 1:1 complexes in solution. In other cases, although the molar conductance does not show any tendency for leveling off even at a molar ratio of about 4, the corresponding molar ratio data show a considerable change in their slopes at a molar ratio of about one, emphasizing the formation of some weaker 1:1 complex.

The formation constants of all DC24C8– M^+ complexes in different solvent mixtures at various temperatures, obtained by computer fitting of the molar conductance–mole ratio data [28], are listed in Table 1. A sample computer fit of the molar ratio data is shown in Fig. 3. 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 the calculation of formation constants, the association between M^+ and ClO_4^- ions was considered negligible, under the highly dilute experimental conditions used (5.0×10^{-5} M). Furthermore, since the concentration of crown ethers was kept below 1.0×10^{-3} M during the conductometric titrations, the corrections

Fig. 1 Molar conductance ($S\text{ cm}^2\text{ mol}^{-1}$) vs. $[\text{DC24C8}]/[\text{M}^+]$ for various DC24C8– M^+ systems at 25 °C in different AN–NM mixtures. The M^+ cations are (a) K^+ , (b) Rb^+ , (c) Cs^+ , (d) Tl^+

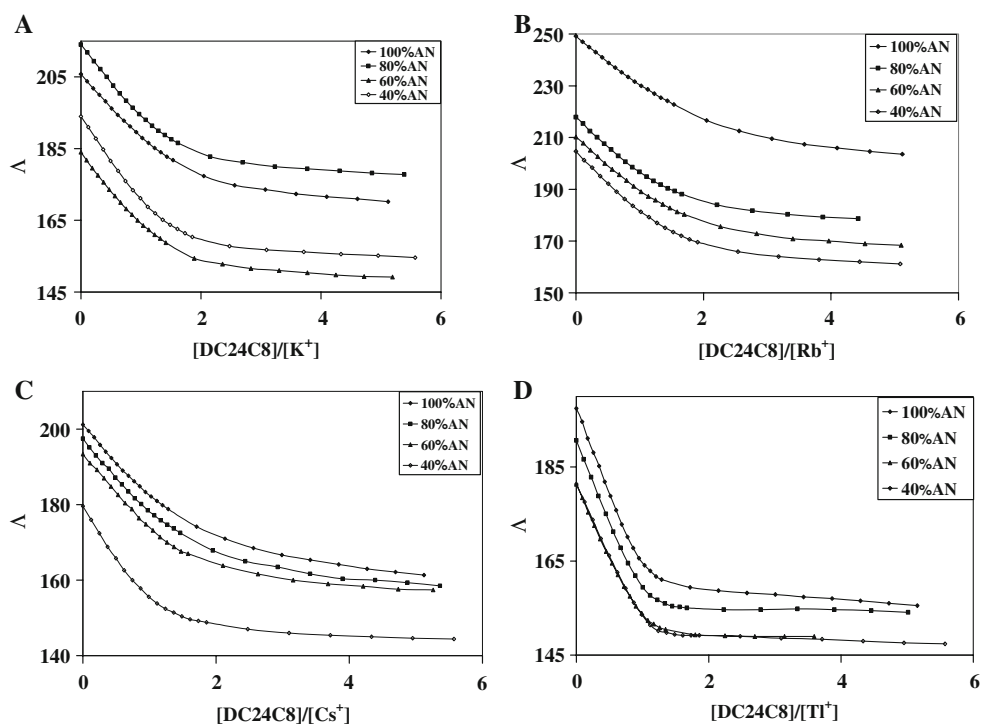
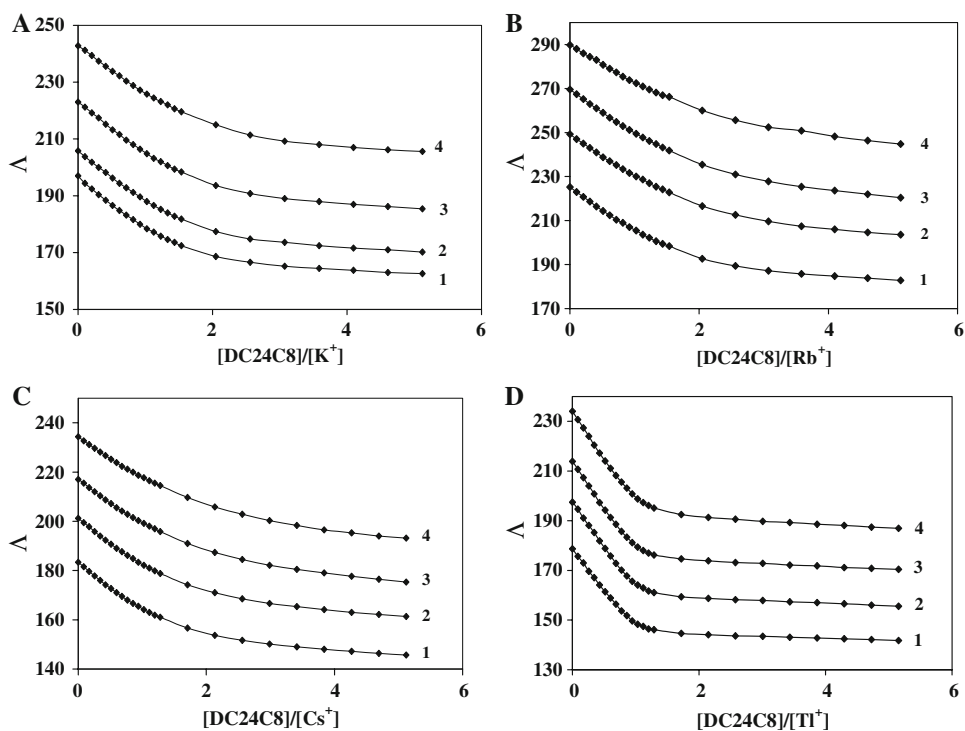


Fig. 2 Molar conductance ($S\text{ cm}^2\text{ mol}^{-1}$) vs. $[\text{DC24C8}]/[\text{M}^+]$ plots in 100% AN at various temperatures: (1) 15 °C, (2) 25 °C, (3) 35 °C, (4) 45 °C. The M^+ cations are (a) K^+ , (b) Rb^+ , (c) Cs^+ , (d) Tl^+



for viscosity changes were also neglected. The formation of complexes between DC24C8 and Rb^+ , Cs^+ and Tl^+ ions in different solvents have already been confirmed by a variety of physicochemical techniques including ^{133}Cs competitive NMR [29, 30] and polarography [19].

In order to have a better understanding of the thermodynamics of complexation reactions of K^+ , Rb^+ , Cs^+ and Tl^+ ions with DC24C8, it is useful to investigate the enthalpic and entropic contributions in these reactions. The ΔH° and ΔS° of the complexation reactions in different AN–NM mixtures were evaluated by the temperature

Table 1 Formation constants, enthalpies and entropies for different M^+ -DC24C8 complexes in various AN–NM mixtures

Cation	wt% AN	Log K_f				ΔH° (kJ mol $^{-1}$)	ΔS° (J mol $^{-1}$ K $^{-1}$)	ΔG° (kJ mol $^{-1}$)
		15 °C	25 °C	35 °C	45 °C			
K^+ (1.38 Å)	100	4.52 ± 0.05	4.42 ± 0.02	4.37 ± 0.02	4.26 ± 0.05	-14 ± 1	36 ± 4	-25 ± 2
	80	4.69 ± 0.09	4.63 ± 0.08	4.51 ± 0.05	4.41 ± 0.09	-17 ± 1	32 ± 5	-26 ± 2
	60	4.68 ± 0.06	4.66 ± 0.05	4.55 ± 0.04	4.43 ± 0.07	-15 ± 3	38 ± 10	-26 ± 4
	40	4.92 ± 0.05	4.78 ± 0.09	4.70 ± 0.05	4.52 ± 0.05	-22 ± 2	16 ± 7	-27 ± 3
Rb^+ (1.52 Å)	100	4.31 ± 0.06	4.13 ± 0.08	4.09 ± 0.04	4.00 ± 0.05	-17 ± 3	22 ± 11	-23 ± 5
	80	4.59 ± 0.04	4.53 ± 0.09	4.38 ± 0.07	4.27 ± 0.06	-19 ± 2	21 ± 7	-25 ± 3
	60	4.55 ± 0.06	4.43 ± 0.05	4.32 ± 0.07	4.19 ± 0.07	-21 ± 1	15 ± 1	-25 ± 1
	40	4.65 ± 0.09	4.57 ± 0.07	4.45 ± 0.07	4.39 ± 0.05	-16 ± 1	34 ± 4	-26 ± 2
Cs^+ (1.67 Å)	100	4.35 ± 0.03	4.25 ± 0.06	4.08 ± 0.09	3.98 ± 0.04	-22 ± 2	5 ± 6	-24 ± 2
	80	4.57 ± 0.07	4.34 ± 0.07	4.25 ± 0.05	4.14 ± 0.02	-24 ± 4	2 ± 13	-25 ± 5
	60	4.67 ± 0.08	4.59 ± 0.06	4.43 ± 0.05	4.38 ± 0.02	-18 ± 2	27 ± 8	-26 ± 3
	40	5.06 ± 0.03	5.07 ± 0.02	4.90 ± 0.02	5.07 ± 0.04	-3 ± 8	87 ± 26	-29 ± 11
Tl^+ (1.54 Å)	100	5.66 ± 0.09	5.47 ± 0.01	5.42 ± 0.01	5.21 ± 0.01	-25 ± 4	23 ± 12	-31 ± 5
	80	5.89 ± 0.01	5.78 ± 0.07	5.62 ± 0.01	5.54 ± 0.02	-21 ± 2	39 ± 6	-32 ± 3
	60	5.88 ± 0.01	5.78 ± 0.01	5.65 ± 0.02	5.53 ± 0.01	-21 ± 1	41 ± 2	-33 ± 1
	40	5.93 ± 0.01	5.84 ± 0.01	5.77 ± 0.02	5.64 ± 0.02	-17 ± 1	55 ± 5	-33 ± 2

^a Ionic radius in parentheses, Ref. [42]

dependence of the formation constants using a linear least-squares analysis according to the Van't Hoff equation. The Van't Hoff plots of $\log K_f$ vs. $1/T$ for different DC24C8- M^+ complexes were linear for all cases studied, as shown in Fig. 4. The enthalpies and entropies of complexation were determined in the usual manner by the slopes and intercepts of the plots, respectively. The results are also included in Table 1.

As is shown in Fig. 5, the variation of stability constants of the DC24C8- M^+ complexes versus the solvent

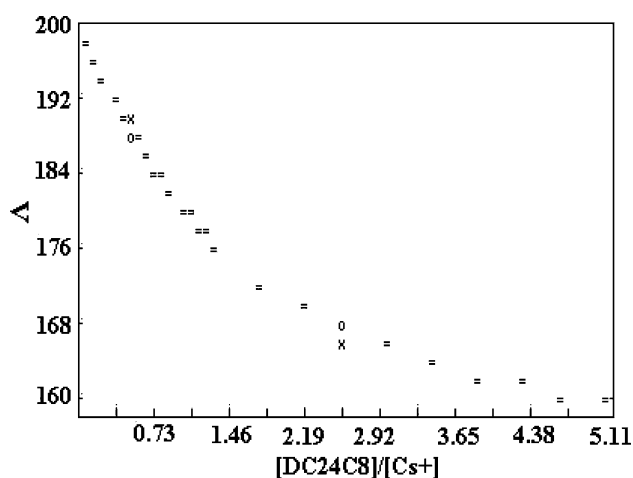


Fig. 3 Computer fit of the molar conductance-mole ratio data for the DC24C8- Cs^+ system at 25 °C in 100% AN: (x) experimental point; (o) calculated point; (=) experimental and calculated points are the same within the resolution of the plot

composition in AN–NM mixtures are not linear. This behavior may be related to changes occurring in the structure of the solvent mixtures and, therefore, changing in the solvation properties of the cyclic polyether, cations and even complexes in these solvent mixtures. Some structural changes probably occur in the structure of the solvents when they mix with one another. These structural changes may result in changing the interactions of those solvents with the solutes. In addition, the heteroselective solvation of the cation, anion and ligand and the characteristics of its changes with the composition of the mixed solvents and temperature may be effective in these complexation processes. In this regard, the interactions between molecules in some mixture solvents have been studied [31].

The data given in Table 1 revealed that, at 25 °C and in all solvent mixtures used, the stability of the 1:1 complexes of DC24C8 with different cations decrease in order of $Tl^+ > K^+ > Rb^+ \sim Cs^+$. 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. Since DC24C8 is too large for the size of the metal ions, the “cation-in-the-hole” model [11] has a limited usefulness in predicting its relative binding capacity with the cations used. In fact, large crown ethers such as DC24C8 are rather flexible ligand that can easily wrap itself around a metal ion of proper size so that all donating oxygen atoms of their ring participate in bond formation. Evidence for the

Fig. 4 Log K_f vs. $1/T$ plots for the 1:1 complexation of K^+ (a), Rb^+ (b), Cs^+ (c) and Tl^+ (d) with DC24C8 in different solvent mixtures

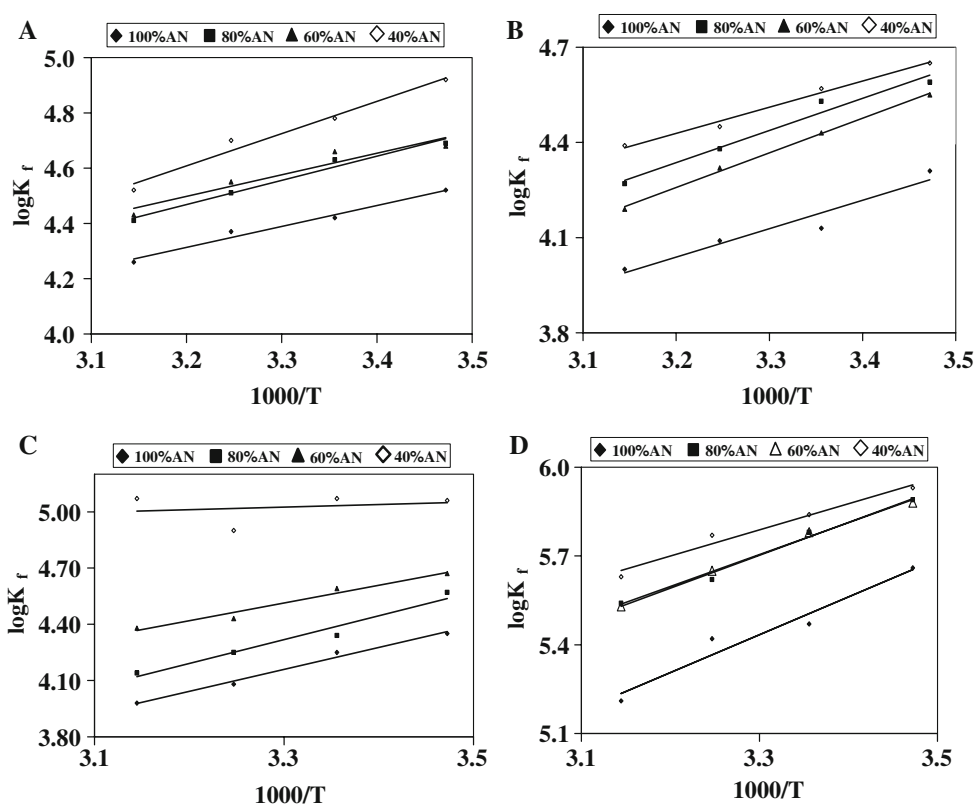
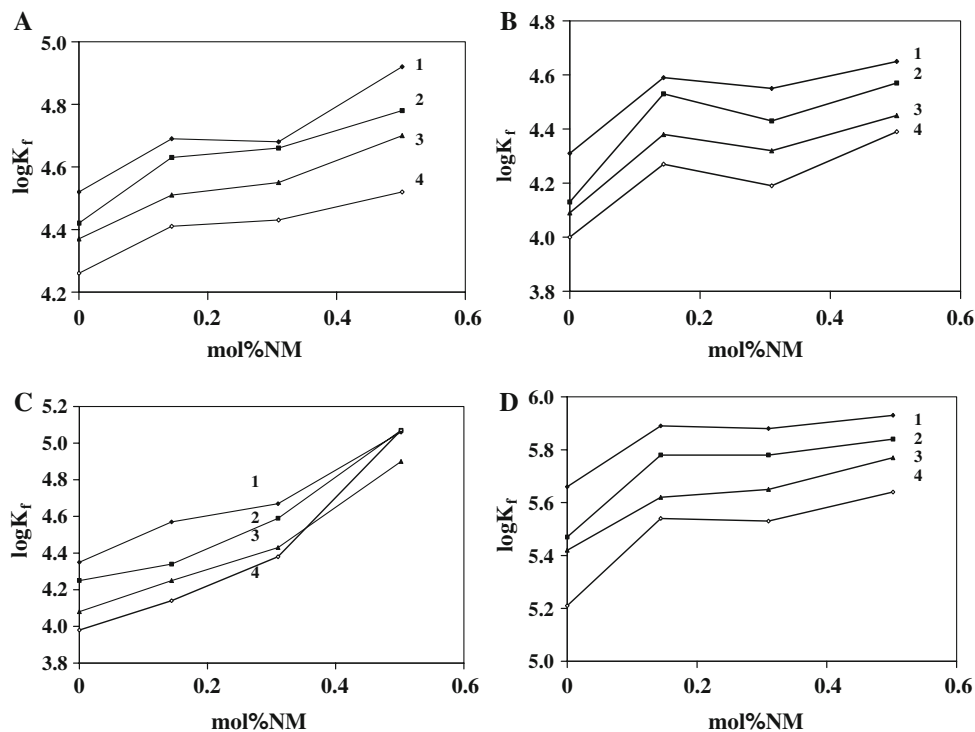


Fig. 5 Variation of the stability constants of various DC24C8– M^+ systems with the composition of the AN–NM binary mixture at different temperatures: (1) 15 °C, (2) 25 °C, (3) 35 °C, (4) 45 °C. The M^+ cations are (a) K^+ , (b) Rb^+ , (c) Cs^+ , (d) Tl^+



existence of such tri-dimensional structures both in solid state [14, 15] and in solution [16–19] has been reported. The data given in Table 1 illustrate that, among different alkali ions studied, the potassium ion forms the most stable

complex with the ligand. In the case of Rb^+ and especially Cs^+ ions, the cations are too large for the formation of a complete “wrap around” structure and, consequently, weaker complexes result.

On the other hand, the monovalent thallium ion is a polarizable metal ion [32], which has been suggested as a probe for potassium ion in biological systems [33]. It can substitute for potassium ion in activation of some important enzymes such as ATPase [34] and pyruvate [35]. Thus, information about the stability and selectivity of Tl^+ complexes with macrocyclic ligands are of special interest in this respect. The increased stability of the Tl^+ -DC24C8 complex over that of K^+ -DC24C8, observed in all solvent mixtures used, is most probably due to the increased polarizability and the more suitable size of thallium ion for the complexation with DC24C8.

The data given in Table 1 clearly illustrate the fundamental role of the solvent properties in the M^+ -DC24C8 complexation reactions studied. Among different factors in solution [11], certainly of vital importance is the ability of solvent molecules to solvate ionic species and thus to compete with the ligands for the cation [16, 37]. Of course, the interaction of some solvents with macrocyclic ligands is of equal importance, although much less appreciated. Thus, the thermodynamic stability of alkali ion-macrocycle complexes is not just a measure of the absolute strength of ion dipole interactions between the cation and the local $-CH_2-O-CH_2-$ groups of the crown ethers [1], but a measure of the relative strength as compared to ionic solvation. In the case of all metal ions studied, the stability of the resulting complexes with DC24C8 increases with increasing weight percent of NM in the solvent mixture. It is well known that the solvating ability of the solvent, as expressed by the Gutmann donor number [23], plays an important role in different complexation reactions [12–26, 36–40]. There is actually an inverse relationship between the stabilities of the complexes and the solvating abilities of the solvents. Nitromethane has a lower donicity ($DN = 2.7$) than acetonitrile ($DN = 14.1$) and, therefore, shows less competition with the crown ether for mentioned ions; thus, it is not unexpected to observe that addition of nitromethane to AN will increase the stability of the complexes.

From comparison of the data given for DC24C8 in Table 1 and for dibenzo-24-crown-8 (DB24C8) in our previous work [41], it is immediately obvious that, in all solvent mixtures used, the complexes with DC24C8 are much more stable than that with the DB24C8. It is well known that the presence of two cyclohexyl groups substituted on the crown ether's cavity can pump electrons into the ligand ring and thus increase the basicity of the oxygen atoms. The result is the increased stability of the cation-crown ether complexes. On the other hand, the addition of two benzo groups to the macrocyclic ring lowers the stability of the complexes markedly. This behavior may be attributed to some combination of the inductive electron withdrawing property of the benzo groups, which weakens the electron-donor ability of the oxygen atoms of the ring,

and reduced flexibility of the ligand which prevents to some extent the macrocyclic molecule warping itself around the cation. Thus, the increased stability of the M^+ -DC24C8 complexes in comparison with the M^+ -DB24C8 complexes is not surprising [37].

Conclusions

From the conductometric results obtained on the thermodynamics of complexation of DC24C8 with K^+ , Rb^+ , Cs^+ and Tl^+ ions in different AN–NM binary mixtures it can be concluded that:

1. For alkali metal ions, the cation size is primarily responsible for their “wrap around” complex formation with such large crown ether as DC24C8, due to their convenient fit inside the twisted conformation of the crown ether.
2. The increased stability of the Tl^+ -DC24C8 complex over that of K^+ -DC24C8, observed in all solvent mixtures used, is most probably due to the increased polarizability of thallium ion, despite its less suitable size of for the complexation with DC24C8.
3. There is an inverse relationship between the stabilities of all the complexes and the solvating abilities of the solvents, as expressed by the Gutmann donor number [23].

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