Conductance Study of the Thermodynamics of Complexation of K^+, Rb^+, Cs^+ and Tl^+ Ions with Dibenzo-24-crown-8 in Binary Acetonitrile–Nitromethane Mixtures

MEHDI TAGHDIRI[1], MOHAMMAD KAZEM ROFOUEI[1] and
MOJTABA SHAMSIPUR[2]*
[1]*Department of Chemistry, Tarbiat Moallem University, Tehran, Iran;* [2]*Department of Chemistry, Razi University, Kermanshah, Iran*

Abstract

The complexation reactions between dibenzo-24-crown-8 (DB24C8) and K^+, Rb^+, Cs^+ and Tl^+ ions were studied conductometrically in 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 the order $Tl^+ > K^+ > Rb^+ > Cs^+$. The enthalpy and entropy changes of the complexation reactions were evaluated from the temperature dependence of formation constants. It was found that the stability of the resulting complexes increased with increasing nitromethane in the solvent mixture. The $T\Delta S°$ vs. $\Delta H°$ plot of all thermodynamic data obtained shows a fairly good linear correlation indicating the existence of enthalpy–entropy compensation in the complexation reactions.

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 [2–5], 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 non-polar 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 [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 non-aqueous solvents have been extensively reported in literature, the complexation reaction of these complexes in mixed solvent systems have been investigated only to a very limited extent [11–13].

Among the macrocyclic polyethers, large crown ethers (i.e., larger than 18-crown-6) possess interesting comploexation 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. Evidences for the formation such three-dimensional structures both in solid state [14, 15] and in solution [16–19] have 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].

It was of interest to us to study the influence of the cation size (and nature) and solvent properties on the interaction of metal ions with large crown ethers.

In this work, we report a conductometric study of the stoichiometry, stability and thermodynamic parameters of the dibenzo-24-crown-8 (DB24C8) 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].

* Author for Correspondence: E-mail: mshamsipur@yahoo.com

Experimental

Reagent-grade potassium perchlorate, dried acetonitrile ($H_2O < 0.005\%$) and DB24C8 (all from Merck) 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 NM (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 triply 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 a 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 DB24C8 and the univalent cations used, in different AN–NM mixtures and at various temperatures, were calculated by fitting the observed molar conductance, Λ_{obs}, at varying [DB24C8]/[M$^+$] mole ratios to a previously derived equation [25, 26] which express the Λ_{obs} as a function of the free and complexed metal ions, and 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 DB24C8 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 vs. DB24C8/cation mole ratio plots are shown in Figures 1 and 2.

As it is seen from Figures 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$^+$–DB24C8 system and in all binary AN–NM mixtures studied, the addition of DB24C8 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 a conductance behavior is indicative of the formation of fairly stable 1:1 complexes in solution. However, 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 DB24C8–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 Figure 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 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 for viscosity changes were also neglected. The formation of such 1:1 complexes between DB24C8 and K$^+$, Rb$^+$, Cs$^+$ and Tl$^+$ ions in different have already been confirmed by a variety of physicochemical techniques including conductometry [29], polarography [19, 30], ^{133}Cs NMR [31], ^{205}Tl NMR [31] and spectrophotometry [32, 33].

In order to have a better understanding of the thermodynamics of complexation reactions of K$^+$, Rb$^+$, Cs$^+$ and Tl$^+$ ions with DB24C8, it is useful to investigate the enthalpic and entropic contributions to these reactions. The $\Delta H°$ and $\Delta S°$ of the complexation reactions in different AN–NM mixtures 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 vs. $1/T$ for different DB24C8–M$^+$ complexes were linear for all cases studied, as shown in Figure 4. 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 also included in Table 1.

It is interesting to note that the formation constants obtained in this study at 25 °C in pure acetonitrile are in satisfactory agreement with the previously reported corresponding values, and obtained by different physicochemical methods, in the literature, within the experimental errors reported. These are log K_f = 3.55 ± 0.09
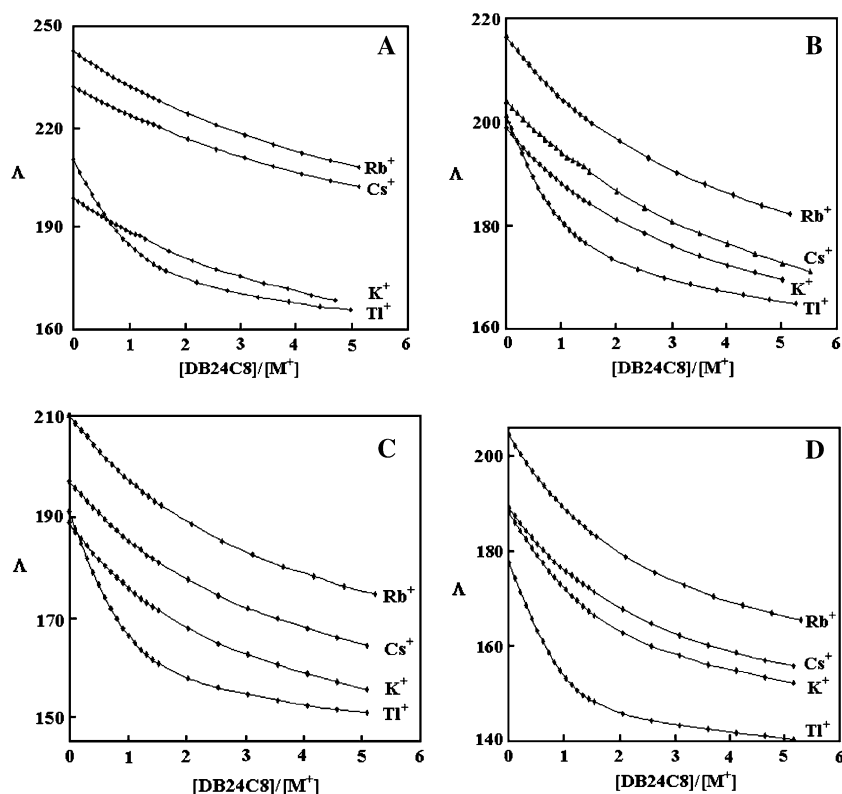
Figure 1. Molar conductance (S cm^2 mol^{-1}) vs. [DB24C8]/[M$^+$] for various DB24C8–M$^+$ systems at 25 °C in different AN–NM mixtures. Weight percent of AN in the binary mixtures are: (A) 100%, (B) 80%, (C) 60%, (D) 40%.

for K$^+$ against 3.70 ± 0.05 by polarography [30]; log $K_f = 3.56 \pm 0.02$ for Rb$^+$ against 3.40 ± 0.05 by polarography [30], log $K_f = 3.49 \pm 0.03$ for Cs$^+$ against 3.94 ± 0.07 by ^{133}Cs NMR [31] and log $K_f = 4.63 \pm 0.04$ for Tl$^+$ against 4.81 ± 0.05 by ^{205}Tl NMR [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 DB24C8 with different cations decrease in the order Tl$^+$ > K$^+$ > Rb$^+$ > Cs$^+$. It is interesting to note that a similar stability order for alkali metal ion complexation with DB24C8 in pure nitromethane has already been reported in the literature [34]. 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 DB24C8 has a cavity (with a radius of > 2 Å) [35] 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 DB24C8 are rather flexible ligand that can be easily wrap itself around a metal ion of proper size so that all donating oxygen atoms of their ring participate in bond formation. Evidences for the existence of such tri-dimensional structures both in solid state [14, 15] and in solution [16–19] have been reported. The data given in Table 1 illustrate that, among different alkai 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 a complete ''wrap around'' structure and, consequently, weaker complexes result.

On the other hand, the monovalent thallium ion is a polarizable metal ion [36], which has been suggested as a probe for potassium ion in biological systems [37]. It can substitute for potassium ion in activation of some important enzymes such as ATPase [38] and pyruvate [39]. 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$^+$–DB24C8 complex over that of K$^+$–DB24C8, observed in all solvent mixtures used, is most probably due to the increased polarizability thallium ion, despite its less suitable size of for the complexation with DB24C8.

The data given in Table 1 clearly illustrate the fundamental role of the solvent properties in the M$^+$–DB24C8 complexation reactions studied. In the case of all metal ions studied, the stability of the resulting complexes with DB24C8 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, 28–33]. 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
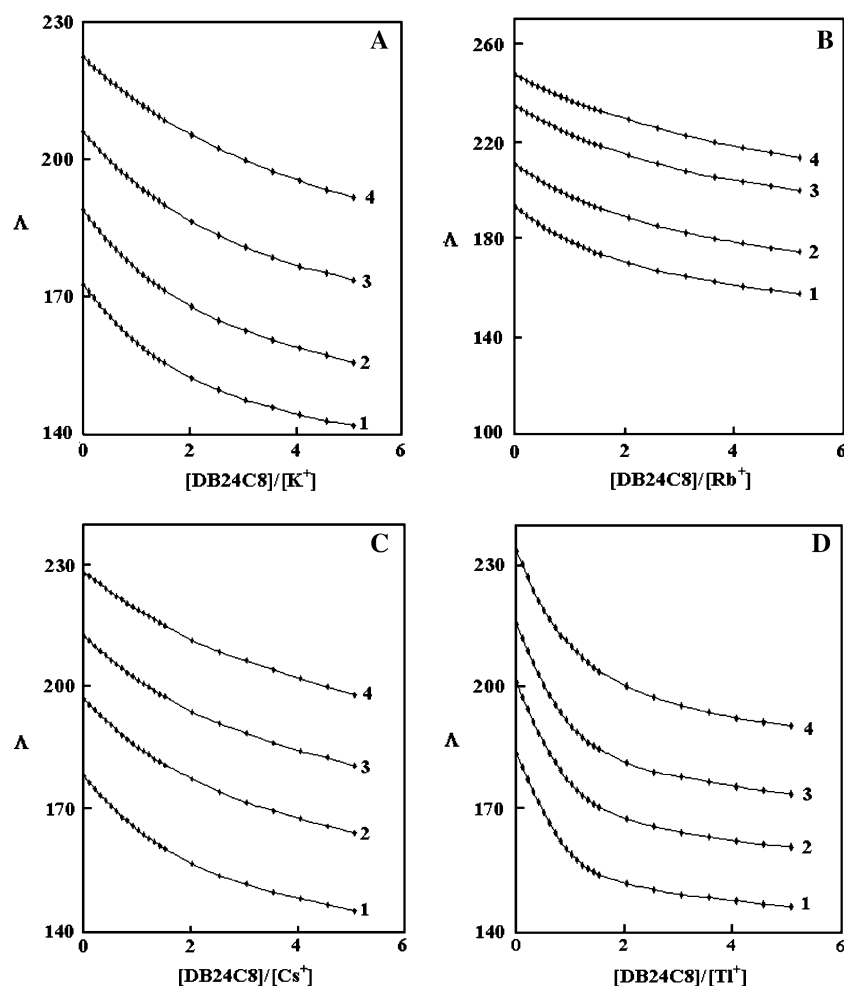
Figure 2. Molar conductance (S cm² mol⁻¹) vs. [DB24C8]/[M⁺] plots in 60% AN at various temperatures: (1) 15 °C, (2) 25 °C, (3) 35 °C, (4) 45 °C. The M⁺ cations are (A) K⁺, (B) Rb⁺, (C) Cs⁺, (D) Tl⁺.

ether for mentioned ions; thus, it is not unexpected to observe that addition of nitromethane to AN will increase the stability of the complexes.

Table 1 shows that, as expected, for all M⁺–DB24C8 systems studied, the thermodynamic data vary significantly with the solvent properties.

Table 1. Formation constants, enthalpies and entropies for different M⁺–DB24C8 complexes in various AN–NM mixtures

Cation	wt% AN	Log K_f				$\Delta H°$ (kJ mol⁻¹)	$\Delta S°$ (J mol⁻¹ K⁻¹)	$\Delta G°$ (kJ mol⁻¹)
		15 °C	25 °C	35 °C	45 °C			
K⁺ (1.38 Å)	100	3.66 ± 0.05	3.55 ± 0.09	3.14 ± 0.05	2.75 ± 0.06	−53 ± 5	−113 ± 16	−19 ± 7
	80	4.04 ± 0.03	3.88 ± 0.03	3.75 ± 0.02	3.63 ± 0.03	−24 ± 1	−6 ± 4	−22 ± 2
	60	4.09 ± 0.02	3.99 ± 0.03	3.85 ± 0.02	3.65 ± 0.02	−25 ± 3	−10 ± 9	−23 ± 4
	40	4.38 ± 0.04	4.23 ± 0.04	4.12 ± 0.03	4.00 ± 0.03	−22 ± 1	8 ± 3	−24 ± 1
Rb⁺ (1.52 Å)	100	3.67 ± 0.04	3.56 ± 0.02	3.26 ± 0.04	2.94 ± 0.05	−43 ± 6	−79 ± 20	−20 ± 9
	80	3.92 ± 0.03	3.83 ± 0.04	3.63 ± 0.05	3.50 ± 0.04	−26 ± 2	−13 ± 8	−22 ± 3
	60	4.04 ± 0.05	3.89 ± 0.04	3.78 ± 0.04	3.63 ± 0.03	−23 ± 1	−4 ± 3	−22 ± 1
	40	4.18 ± 0.03	4.04 ± 0.03	3.93 ± 0.08	3.83 ± 0.04	−20 ± 1	9 ± 4	−23 ± 2
Cs⁺ (1.67 Å)	100	3.77 ± 0.03	3.49 ± 0.03	3.37 ± 0.03	3.14 ± 0.02	−37 ± 1	−55 ± 5	−20 ± 2
	80	3.76 ± 0.03	3.62 ± 0.05	3.40 ± 0.03	3.14 ± 0.05	−38 ± 4	−26 ± 14	−30 ± 6
	60	4.04 ± 0.08	3.87 ± 0.03	3.77 ± 0.01	3.61 ± 0.03	−24 ± 2	−3 ± 5	−23 ± 2
	40	4.14 ± 0.02	3.99 ± 0.03	3.85 ± 0.06	3.70 ± 0.03	−26 ± 1	−4 ± 1	−24 ± 1
Tl⁺ (1.54 Å)	100	4.76 ± 0.04	4.63 ± 0.04	4.49 ± 0.04	4.35 ± 0.06	−24 ± 1	3 ± 1	−25 ± 1
	80	4.74 ± 0.03	4.60 ± 0.04	4.42 ± 0.03	4.30 ± 0.04	−26 ± 1	−0.2 ± 4	−26 ± 2
	60	4.95 ± 0.03	4.79 ± 0.04	4.74 ± 0.03	4.53 ± 0.04	−23 ± 4	7 ± 12	−25 ± 5
	40	5.00 ± 0.02	4.92 ± 0.02	4.86 ± 0.02	4.74 ± 0.03	−15 ± 1	20 ± 5	−20 ± 2

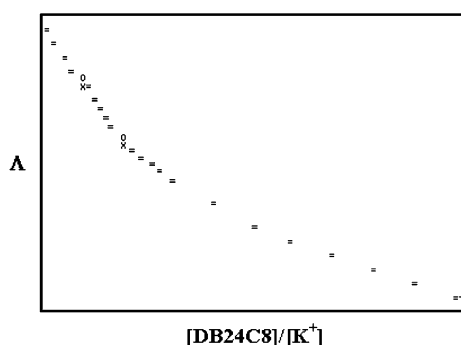ᵃIonic radius in parentheses, Ref [43].

Figure 3. Computer fit of the molar conductance–mole ratio data for the DB24C8–K$^+$ system at 25 °C in 60% AN: (×) experimental point; (○) calculated point; (=) experimental and calculated points are the same within the resolution of the plot.

Figure 5. Plot of TΔS° (kJ mol^{-1}) vs. ΔH° (kJ mol^{-1}) for 1:1 complexation of K$^+$, Rb$^+$, Cs$^+$ and Tl$^+$ ions with DB24C8 in different AN–NM binary mixtures.

However, in all cases, the observed increase (or decrease, depending on the nature of the metal ion) in ΔH° value upon addition of NM to the solvent mixture will be compensated by an increase (or decrease) in the corresponding ΔS° value. The existence of such a compensating effect (Figure 5) between ΔH° and ΔS° values, which has been frequently reported for a variety of metal–ligand systems [40–43], would cause 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.

Conclusions

From the cunductomeric results obtained on the thermodynamics of complexation of DB24C8 with K$^+$, Rb$^+$, Cs$^+$ and Tl$^+$ ions in different AN–NM binary mixtures it can be concluded that:
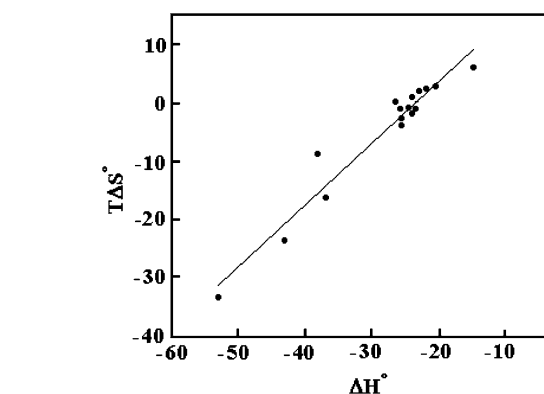
1. For alkali metal ions, the cation size is primarily responsible for their "wrap around" complex formation with such a large crown ether as DB24C8, due to their convenient fit inside the twisted conformation of the crown ether.
2. The increased stability of the Tl$^+$–DB24C8 complex over that of K$^+$–DB24C8, 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 DB24C8.
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].
4. Although the enthalpy and entropy changes are strongly solvent dependent, the observed increase (or decrease, depending on the nature of the metal ion) in ΔH° value upon addition of NM to AN will be compensated by an increase (or decrease) in the corresponding ΔS° value.
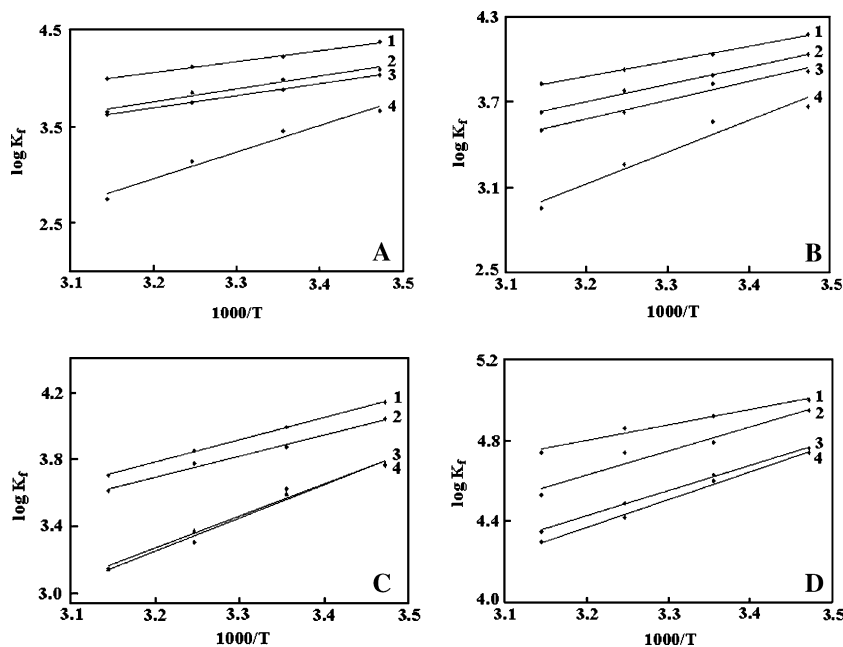

Figure 4. Log K_f vs. $1/T$ plots for the 1:1 complexation of K$^+$ (A), Rb$^+$ (B), Cs$^+$ (C) and Tl$^+$ (D) with DB24C8 in different solvent mixtures: (1) 40%AN, (2) 60%AN, (3) 80%AN, (4) 100% AN.

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