



A Polarographic Study of Tl^+ , Pb^{2+} and Cd^{2+} Complexes with Dicyclohexano-18-Crown-6 in Some Binary Mixed Solvents

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(Received: 27 November 2001; in final form: 17 May 2002)

Key words: dicyclohexano-18-crown-6, Pb^{2+} , Tl^+ , Cd^{2+} , mixed solvents, polarography metal complexes, stability constants

Abstract

The complexes of Tl^+ , Pb^{2+} and Cd^{2+} cations with the macrocyclic ligand, dicyclohexano-18-crown-6 (DC18C6) were studied in water/methanol ($H_2O/MeOH$), water/1-propanol ($H_2O/1-PrOH$), water/acetonitrile (H_2O/AN), water/dimethylformamide (H_2O/DMF), dimethylformamide/acetonitrile (DMF/AN), dimethylformamide/methanol (DMF/MeOH), dimethylformamide/1-propanol (DMF/1-PrOH) and dimethylformamide/nitromethane (DMF/NM) mixed solvents at 22 °C using differential pulse polarography (DPP), square wave polarography and conductometry. In general, the stability of the complexes was found to decrease with increasing concentration of water in aqueous/non-aqueous mixed solvents with an inverse relationship between the stability constants of the complexes and the concentration of DMF in non-aqueous mixed solvents. The results show that the change in stability of DC18C6. Tl^+ , vs the composition of solvent in DMF/AN and DMF/NM mixed solvents is apparently different from that in DMF/MeOH and DMF/1-PrOH mixed solvents. While the variation of stability constants of the DC18C6. Tl^+ and DC18C6. Pb^{2+} complexes vs the composition of H_2O/AN mixed solvents is monotonic, an anomalous behavior was observed for variations of $\log K_f$ vs the composition of $H_2O/1-PrOH$ and $H_2O/MeOH$ mixed solvents. The selectivity order of the DC18C6 ligand for the cations was found to be $Pb^{2+} > Tl^+ > Cd^{2+}$.

Introduction

The stability and selectivity of crown ether complexes with metal ions depend on several molecular factors. These include the cavity size of the ligand, the character of the heteroatoms in the polyether ring, the spatial distribution of ring binding sites, the charge density and polarizability of the cation and the cation diameter [1–3]. One of the major factors is also the type of solvent used in complexation reactions. The influence of the solvent on the complexation of cations by macrocyclic ligands is not restricted to the solvation of the cation, but the interaction between the ligand and solvent molecules and the solvation of the resulting complex may also play an important role in complexation reactions [4–5]. As a result, the stability and selectivity of complexes can be greatly altered by changing the solvent properties [6].

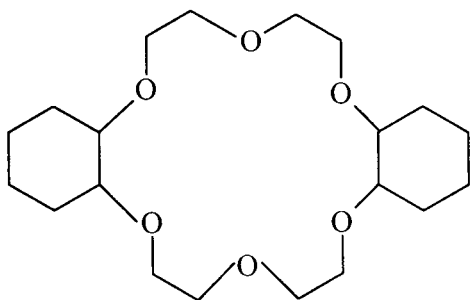
The physicochemical properties of mixed solvents are interesting both from a theoretical and practical point of view, because many chemical and electrochemical reactions might be carried out advantageously in these media. Usually mixed solvents do not behave as expected from statistical considerations, the solvating ability of solvents in mixtures can be different from those of neat media [7]. The deviations from ideal behavior are indicative of the extent of preferential solvation and the existence of specific solvent – solute and solvent – solvent interactions [8–11].

Although the complexation of crown ethers with metal cations has been extensively studied in both aqueous and non-aqueous solvents, most of these investigations have been restricted to neat solvents [12–15] and the data about the stability constants of crown ether complexes with metal ions in mixed solvents is very sparse [16]. Much more attention has been paid to the complexation of alkali and alkaline earth metal ions by macrocyclic ligands [17–22] and little attention has been paid to heavy metal ion complexes, particularly in mixed solvent systems [23].

While the complexes of Tl^+ , Pb^{2+} and Cd^{2+} cations with some of the crown ethers have been studied in a wide variety of neat solvents [see Refs. 2, 3, and corresponding references therein], the available information on such complexes in mixed solvents is very sparse [24–28].

We have reported previously the results obtained on the complexation of the alkali and a few heavy metal ions with some crown ethers in several mixed solvents [29–32]. We have now extended these studies to complex formation between DC18C6 (Scheme 1) and Tl^+ , Pb^{2+} and Cd^{2+} ions in $H_2O/MeOH$, $H_2O/1-PrOH$, H_2O/AN , H_2O/DMF and DMF/AN, DMF/MeOH, DMF/1-PrOH and DMF/NM systems in order to see how the variation in the nature and composition of the solvent and the relative size and type of the cation affect the stability and selectivity of complexation. Several solvents with a wide range of donor number (DN) and dielectric constant have been selected for preparing the

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Scheme 1. Dicyclohexano-18-crown-6.

mixed solvents. The three heavy metal ions were selected as probe cations, because they are very toxic [33, 34], hence, evaluation of reaction conditions and design of a highly selective ligand for removal of these harmful cations is very important.

Among the various physicochemical methods which are used for the study of cation-crown ether complexes [2–3], polarography is a very useful means for studying the electrochemical behavior of macrocyclic complexes. By using this technique, the stoichiometry, stability and selectivity of a number of metal ion complexes in both aqueous and non-aqueous media have been determined [35–40].

Experimental

Reagents

Dicyclohexano-18-crown-6 (DC18C6) (Merck) was used without further purification except for drying over P_2O_5 in vacuum for 72 h. Reagent-grade thallium(I)nitrate, lead(II)nitrate and cadmium(II)nitrate (all from Merck) and tetraethylammonium perchlorate, TEAP (Merck) were used as received except for drying over P_2O_5 in vacuum for 48 h.

The solvents, dimethylformamide, acetonitrile, methanol and nitromethane (all from Merck) and 1-propanol (Riedel) with the highest purity and triply-distilled water were used for preparation of the desired mixed solvents.

Apparatus

The polarographic measurements i.e. differential pulse polarography (DPP), square wave polarography (SWP) and cyclic voltammetry (CV) were carried out on an EG&G Princeton Applied Research (PAR), 384B polarographic analyzer with a static mercury drop electrode (SMDE) in a three-electrode arrangement (EG&G PAR 303A). A Pt wire with a considerably larger surface area than that of the SMDE was used as an auxiliary electrode. A Ag/AgCl reference electrode with a bridge containing the base electrolyte of the electrolysed solution was employed. A solution of 0.025 M tetraethylammonium perchlorate (TEAP) was used as a base electrolyte. All solutions were deaerated for 10 minutes with pure helium and a helium atmosphere was maintained over the solutions during the reduction.

The usual instrumental parameters were pulse height, 20 mV; drop step time, 0.50 s; scan rate, 4.0 mVs⁻¹ and

pulse duration, 0.040 s for the DPP experiments and pulse height, 20 mV; equilibration time, 5 s; scan rate, 200 mVs⁻¹ for the SWP experiments. All experiments were carried out at 22 ± 0.5 °C. The conductometric experiments were performed using a digital Amel conductivity apparatus, model 60, in a water-bath thermostated at 22 ± 0.5 °C.

Procedure

The stability constants of metal ion-crown ether complexes in different solvent mixtures were determined based on the measurement of the shift in E_p (peak potential) caused by addition of an increasing amount of the ligand. The shift in half-wave (or peak) potential towards more negative values upon addition of an excess amount of ligand was found to be in accordance with the Lingane equation [41]:

$$\begin{aligned} \Delta E_{1/2} &= (E_{1/2})_{\text{complex}} - (E_{1/2})_{\text{metal}} \\ &= \left(-\frac{RT}{nF}\right)(\ln K_f + \rho \ln [L]_t) \end{aligned} \quad (1)$$

where $(E_{1/2})_{\text{complex}}$ and $(E_{1/2})_{\text{metal}}$ are the half-wave potentials of the complexed and free metal ion, n is the number of electrons transferred, K_f is the stability constant of the complex, ρ is the stoichiometry of the complex and $[L]_t$ is the analytical concentration of the ligand. The ρ and $\log K_f$ values were obtained from the slope and intercept of the linear plots of $\Delta E_{1/2}/-2.303(RT/nF)$ versus $\log [L]_t$, respectively.

The experimental procedure for obtaining the stability constants of complexes using the conductometric method is described in Ref. 25.

Results and discussion

In a polarographic investigation of complexation of metal ions by ligands, the difference between the half-wave potentials ($E_{1/2}$) or the differential pulse peak potential (E_p) of the free and complexed metal ion is a measure of the complex stability [42].

The complexation reactions of DC18C6 ligand with Tl^+ , Pb^{2+} and Cd^{2+} cations were studied in DMF/NM, DMF/AN, DMF/1-PrOH, DMF/MeOH, H₂O/MeOH, H₂O/1-PrOH, H₂O/AN and H₂O/DMF mixed solvents using DPP, SWP and conductometry at 22 °C. The polarographic results show that addition of the ligand to Tl^+ , Pb^{2+} and Cd^{2+} solutions in 0.025 M tetraethylammonium perchlorate, shifts the differential pulse peak potential (E_p) for the reduction of the complexed ions towards more negative values. As an example, the differential pulse polarograms of the Tl^+ ion in different concentrations of DC18C6 in a H₂O/1-PrOH mixed solvent (mol% of water = 51.03) are shown in Figure 1. Similar polarograms were obtained for the other systems.

The reversibility of the systems was studied by CV, the cyclic voltammograms show that the reduction of Tl^+ in the presence of ligand is reversible in all of the mixed solvents used in these studies. As an example, a cyclic voltammogram of the DC18C6. Tl^+ complex in DMF/H₂O mixed

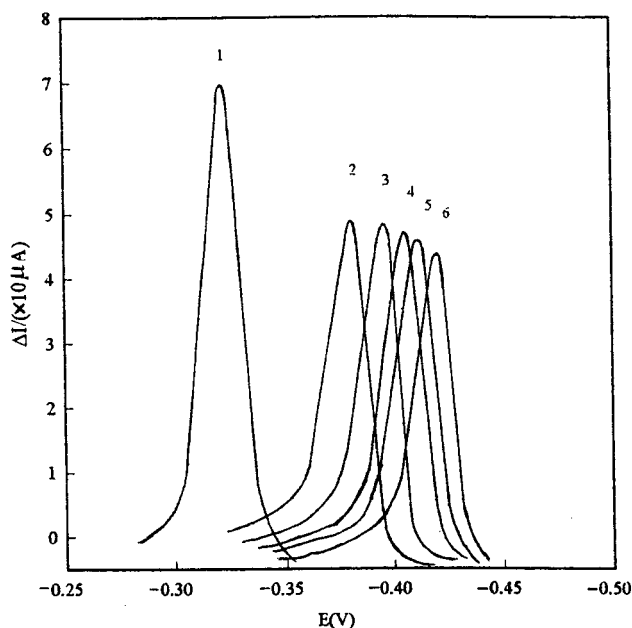


Figure 1. Differential pulse polarograms of 0.01 mM Tl^+ ion in 1-propanol/water (mol% of water = 51.03) binary mixture with different concentration of the DC18C6 ligand. Concentration of DC18C6/mM: (1) 0; (2) 0.5; (3) 1; (4) 1.4; (5) 1.9; (6) 2.3.

solvent (mol% of water = 51.88) which indicates the reversible electrochemical behavior of the complex is illustrated in Figure 2. As seen from Tables 1 and 2, the reduction of the DC18C6. Pb^{2+} and DC18C6. Cd^{2+} complexes is irreversible in some of the binary mixed and neat solvent systems.

The variation of $\Delta E_{1/2} / -2.303(RT/nF)$ as a function of $\log [DC18C6]_t$ for the complex formation between DC18C6 and Tl^+ ion in DMF/MeOH mixed solvents is shown in Figure 3. The slopes of the linear plots were close to 1, indicating the formation of a ML complex in solution. Similar behavior was observed for most of the other systems. In the case of aqueous/non-aqueous mixed solvents, in water-rich regions of binary mixtures, a value close to 0.5 was obtained from the slope of the linear plots.

The stability constants of the complexes were obtained by fitting the polarographic data to Equation (1) and the results are listed in Tables 1 and 2. It is seen from Tables 1 and 2, that in all of the mixed solvents, the stability of DC18C6. Pb^{2+} is much higher than that of DC18C6. Tl^+ . Pb^{2+} , with the least soft character [43] and with a good fit condition (ionic size of Pb^{2+} ion is 2.40 Å [44]) can attain a more convenient fit condition than the Tl^+ (2.90 Å [44]) ion for the ligand cavity (cavity size 2.8 Å [45]), moreover, the Pb^{2+} ion bears a high charge density which results in a strong interaction with the ligand. Additionally, the greater polarization and the increased nature of the covalent bonding of the Pb^{2+} ion also explain the higher value of the stability constant of the DC18C6. Pb^{2+} complex than that of the other two complexes. As seen from Tables 1 and 2, the Cd^{2+} ion forms the least stable complex with DC18C6 compared with the Pb^{2+} and Tl^+ ions. This is because the cation size of Cd^{2+} (1.90 Å [44]) is too small to match the ligand cavity

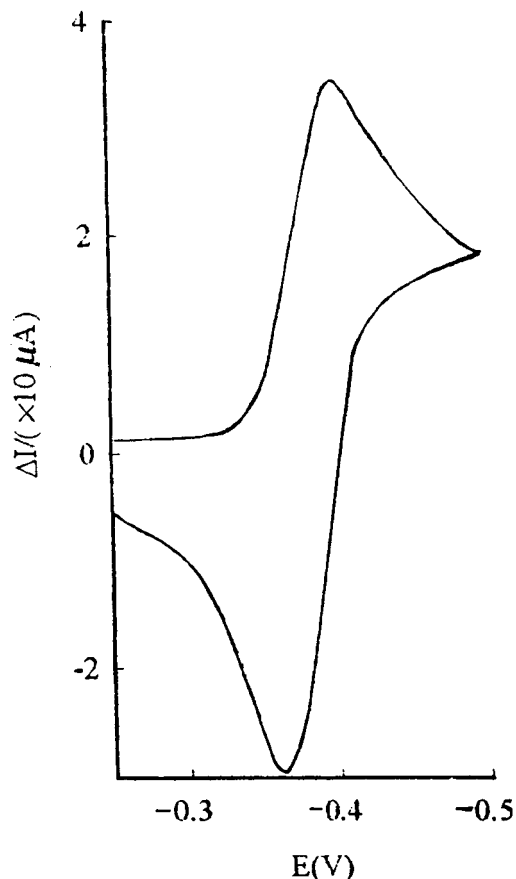


Figure 2. Cyclic voltammogram of the DC18C6. Tl^+ complex in dimethylformamide/water (mol% of water = 51.80) mixture.

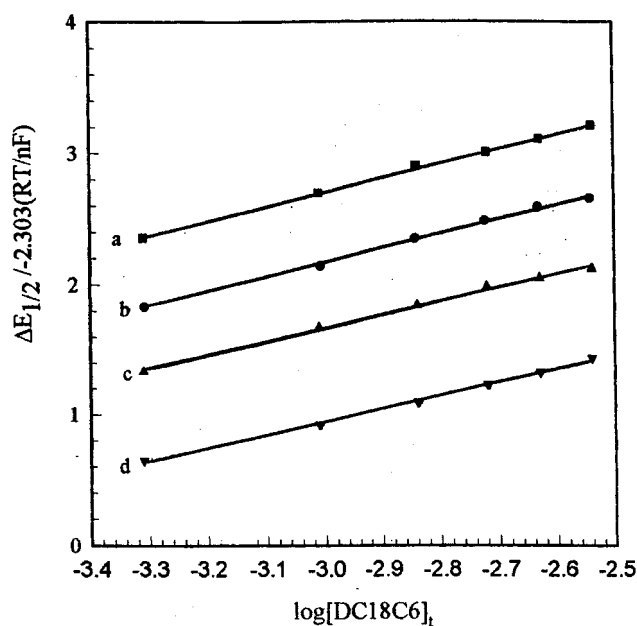


Figure 3. Linear plots of $\Delta E_{1/2} / -2.303(RT/nF)$ vs $\log [DC18C6]_t$ for the DC18C6. Tl^+ complex in methanol/dimethylformamide binary systems. Respective mol% of dimethylformamide: a (11.61), b (25.90), c (44.04), d (65.49).

Table 1. Log K_f values of Tl^+ , Pb^{2+} and Cd^{2+} complexes with DC18C6 in some binary mixed non-aqueous solvents at 22 °C using the SWP technique

Medium	Solvent composition mol% of DMF	^a Log K_f		
		^b Tl^+	^b Pb^{2+}	^b Cd^{2+}
DMF-MeOH	11.61	6.0	i	i
	25.90	5.5	i	i
	44.04	4.8	i	i
	65.49	4.0	i	i
	100	3.2	3.9	i
DMF-(1-PrOH)	19.55	5.8	i	i
	39.31	5.0	i	<2
	59.33	4.4	5.6	<2
	79.54	3.7	3.9	<2
	100	3.2	3.9	i
DMF-AN	14.46	6.0	8.1	4.0
	31.09	4.4	6.2	2.7
	50.32	3.5	4.7	i
	72.30	3.4	4.2	i
	100	3.2	3.9	i
DMF-NM	14.79	6.7	i	i
	31.60	5.0	i	i
	50.98	3.9	i	i
	73.40	3.6	4.7	i
	100	3.2	3.9	i

^aStandard deviations = ± 0.1 .

^bThe concentration of metal ions 1.0×10^{-5} M.

i = irreversible.

Table 2. Log K_f values of Tl^+ and Pb^{2+} complexes with DC18C6 in some binary mixed aqueous/non-aqueous solvents at 22 °C using the DPP technique

Medium	Solvent composition mol% of H ₂ O	^a Log K_f	
		^b Tl^+	^b Pb^{2+}
H ₂ O-DMF	0.0	3.2 (3.30) ^c	3.9 (3.60)
	51.80	3.7 (3.71)	4.9 (4.64)
	74.12	3.4 (3.52)	i (4.53)
	86.57	2.9 (3.09)	i (4.30)
	94.49	2.6	i (4.10)
	100	i	i (3.78)
H ₂ O-MeOH	36.04	4.7	i
	53.03	3.9	i
	60.09	2.6	i
	77.17	1.8	i
	90.01	1.2	i
H ₂ O(1-PrOH)	51.03	4.2	6.1
	73.58	3.4	4.7
	86.24	3.8	5.6
	94.35	1.6	5.0
H ₂ O-AN	48.54	4.5	7.3
	65.97	3.0	6.5
	81.33	2.2	5.9
	92.07	0.8	5.0

^a Standard deviations = ± 0.1 and ± 0.05 for polarographic and conductometric data, respectively.

^b The concentration of metal ions 1.0×10^{-5} M.

^c The figures in parentheses were obtained by the conductometric method.

i = irreversible.

and it also has a higher soft character than the other two cations [43].

The data given in Table 1 show clearly the important influence of the solvent properties on the stability of the complexes. In all of the mixed solvents, the stability of the complexes decreases with increasing concentration of dimethylformamide in the mixed solvents. This behavior can be attributed to the inherent solvating ability of the neat solvents which form the mixture. It has been shown that the solvating ability of a solvent, as expressed by the Gutmann donicity scale [46], plays a fundamental role in complexation reactions. In a solvent with high solvating ability (high donor number), such as DMF (DN = 26.6), the complex formation tends to be weak, since the solvent strongly competes with the ligand for the cation, but in solvents with lower donicity such as acetonitrile (DN = 14.1), methanol (DN = 20), nitromethane (DN = 2.7) and 1-PrOH (DN = 18), the relatively poorer solvating ability of these solvents leads to an increase in the stability constant, therefore, it is reasonable to expect that the stability constant of the complexes increases when the concentration of these solvents is increased in the mixed solvents.

The variation of the stability constant of the DC18C6. Tl^+ complex as a function of the composition of the mixed solvents is shown in Figure 4. It is interesting to note that the change in stability of the DC18C6. Tl^+ complex vs the composition of solvent in DMF/AN and DMF/NM mixed solvents is apparently different from that in DMF/MeOH and DMF/1-PrOH mixed solvents. As is evident from this Figure, when the concentration of DMF increases in DMF/NM and DMF/AN mixed solvents, the stability constant of the complex first decreases rapidly to about 50 mol% of DMF, and then decreases smoothly, whereas in the case of DMF/MeOH and DMF/1-PrOH mixed solvents, the stability constants decrease monotonically as the DMF concentration is increased in these mixed solvents. Similar behavior has been observed for the 18C6. Tl^+ complex in DMF/NM mixed solvents [26]. It is reasonable to assume that the observed behavior in DMF/AN and DMF/NM mixed solvents may be due to some kind of solvent-solvent interactions between these dipolar aprotic solvents when they are mixed with one another. The preferential solvation of the cations in these mixed solvents may be another reason for this kind of behavior. In addition, there is some information about the interaction between crown ethers and solvent molecules in non-aqueous solvents [4–5], therefore, it may be concluded that the solvent-ligand interactions can also exert such effect on the stability constant of the complexes. The influence of the solvent-ligand interactions on the stability constants has also been reported for the complexes of 18-crown-6 with alkali ions in acetonitrile solutions [47].

As is evident from Table 1, the stability of the DC18C6. Tl^+ complex in DMF/AN and DMF/NM mixed solvents is lower than in DMF/MeOH and DMF/1-PrOH mixed solvents. This behavior seems to be unexpected, if we only consider the donicity of the solvents. Since the donor numbers of AN and NM are lower than those of 1-PrOH and

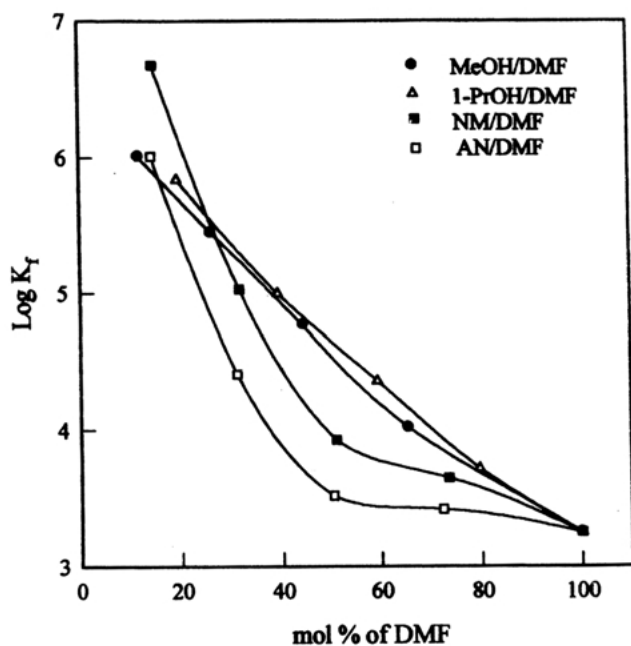


Figure 4. Variation of $\log K_f$ of the DC18C6.Tl⁺ complex in various binary mixtures of dimethylformamide with acetonitrile, nitromethane, methanol and 1-propanol.

MeOH, it is expected that the stability of the complex should be in the order DMF/AN (or DMF/NM) > 1-PrOH/DMF > MeOH/DMF. It should be noted, however, that the donicity scale does not take into account the "hard-soft" interactions between the donor and acceptors [48]. The anomalous behavior which is observed in these systems, may be attributed to the presence of the nitrogen atom in acetonitrile and nitromethane molecules; because the nitrogen atom (as a soft base) can strongly interact with Tl⁺ ion as a soft acid and due to this specific interaction between the solvent molecules and the metal ion, the desolvation of the Tl⁺ ion would be difficult. In addition, the solvent-ligand interactions may also exert an influence on the stability constant of the complex [4]. On the other hand, the high dielectric constants of acetonitrile (38.0) and NM (35.9) with respect to 1-propanol (20.1) and methanol (32.6) can exert a decrease in the electrostatic interactions between the ligand and cation, therefore, the complex formation is weakened in AN/DMF and DMF/NM mixed solvents relative to 1-PrOH/DMF and MeOH/DMF mixed solvents.

The stability constants of the complexes in aqueous/non-aqueous mixtures are summarized in Table 2. In general, the stability constants of complexes decrease with increasing concentration of water in the mixed solvents. Addition of water as a solvent with a high solvating ability (DN = 33) to AN, DMF, MeOH and 1-PrOH with relatively poorer solvating ability (DN = 14.1, 26.6, 20.0 and 18.0, respectively), lead to an increase of the solvating ability of the resulting mixed solvents, therefore, the degree of complexation would be decreased as the concentration of water increased in these mixed solvents. In addition, the higher electric constant of water (78.5) compared with the other solvents could also lead to a decrease in the stability constants of complexes.

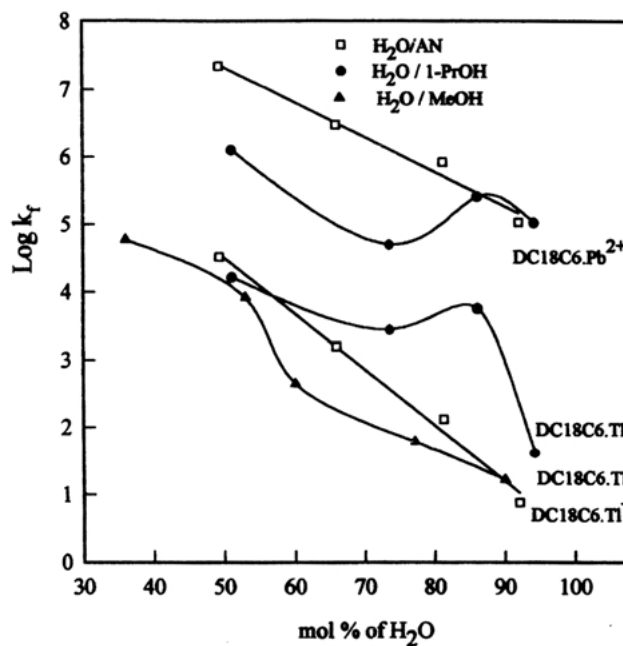


Figure 5. Variation of $\log K_f$ of the DC18C6.Tl⁺ and DC18C6.Pb²⁺ complexes in various binary mixtures of water with acetonitrile, methanol and 1-propanol.

As mentioned before, in some binary aqueous/non-aqueous mixed solvents, the stoichiometry of the DC18C6.Tl⁺ complex is close to 0.5. Since this behavior is only observed in the water rich region of these mixed solvents, it seems that due to the strong solvation of the Tl⁺ ion, the complete desolvation of cation would be difficult and the ligand cannot compete effectively with the solvent molecules, therefore, two partially solvated Tl⁺ ions may be located on both sides of the ligand molecule and hence a M₂L complex is formed which may be considered as an exclusive complex in these mixed solvent systems.

The variations of the stability constant of the DC18C6.Tl²⁺ and DC18C6.Pb²⁺ complexes as a function of solvent composition in H₂O/AN, H₂O/MeOH and H₂O/1-PrOH mixed solvents are shown in Figure 5. As is obvious from this Figure, there is a linear relationship between the $\log K_f$ values and the mole % of water (mol% of H₂O) in H₂O/AN mixed solvents. Similar behavior has also been observed for various complexes in different solvent mixtures [49–51]. This behavior can be attributed to the basicity of these mixed solvents; although the DN values for mixed solvents have not been measured, it has been suggested that the donor number is one of the most widely used empirical parameters of the solvent basicity, particularly in the field of coordination chemistry [52] and it has been shown that in AN/H₂O mixed solvents, the empirical Lewis basicity parameter is monotonically decreased by increasing the amount of water in the mixture [53].

In H₂O/1-PrOH mixed solvents, the variation of the stability constant of the DC18C6.Tl⁺ complex as a function of the mole percent of water is not monotonic (Figure 5). It is interesting to note that a somewhat similar behavior is observed for the DC18C6.Pb²⁺ complex in the same system. In addition, a non-linear behavior is observed for the vari-

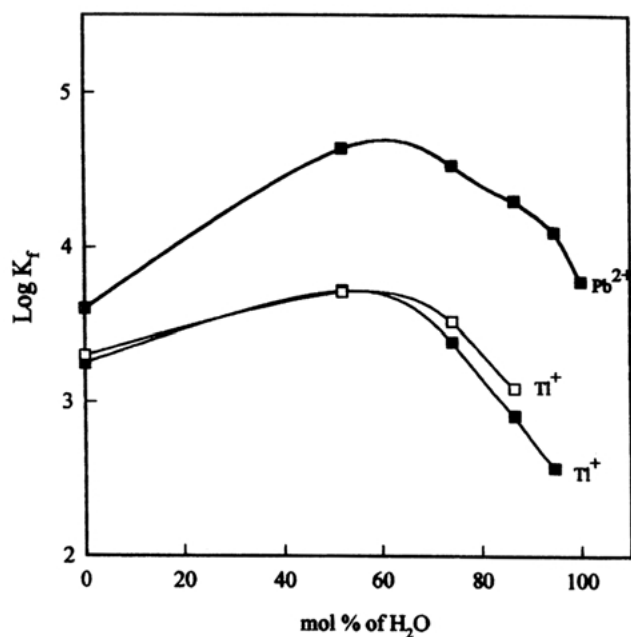


Figure 6. Variation of $\log K_f$ of the DC18C6.Tl⁺ and DC18C6.Pb²⁺ complexes in various binary mixtures of water with dimethylformamide: (■) obtained using the conductometric method, (□) obtained using the polarographic method.

ation of the stability constant of the DC18C6.Tl⁺ complex in H₂O/MeOH mixed solvents. The anomalous behavior which is observed for variations of the stability constants of DC18C6.Pb²⁺ and DC18C6.Tl⁺ complexes vs the composition of the H₂O/1-PrOH and H₂O/MeOH mixed solvents is due to some kind of solvent-solvent interactions in these dipolar protic solvents. It has been shown that the viscosity of these water-alcohol mixtures vs the composition of the mixed solvents passes through a maximum which indicates the strong interaction between water and these alcoholic solvents [54–55].

The results obtained in DMF/H₂O mixed solvents are interesting. As seen from Figure 6, the variations of $\log K_f$ of the DC18C6.Tl⁺ complex in these mixed solvents is not monotonic, the stability constant of the complex first increases on increasing the concentration of water up to about 50 mol% in the mixture and then gradually decreases.

Because of an irreversible behavior of the DC18C6.Pb²⁺ complex in most of these binary mixtures, the $\log K_f$ values of this complex were not obtained using the polarographic technique. In order to obtain more information about these binary mixtures, the $\log K_f$ values for the DC18C6.Pb²⁺ complex were determined using the conductometric method. It is interesting to note that the DC18C6.Pb²⁺ complex behaves in the same manner as the DC18C6.Tl⁺ complex. In addition, as seen from Table 2, the polarographic data are in good agreement with the conductometric results. The observed behavior in these mixed solvents can be related to the changes in the structure of the mixed solvents which may be due to the solvent-solvent interactions between these dipolar protic and dipolar aprotic solvents.

Acknowledgement

The authors gratefully acknowledge the support of this research by the National Research Council of I.R. Iran (NRCI) as a National Research Project under Grant No. 265.

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