Study of Complex Formation Between 18-Crown-6 and Pb^{2+}, Tl^+ and Cd^{2+} Cations in Binary Aqueous/Non-aqueous Solvents Using Polarographic Techniques (DPP and SWP)

GHOLAMHOSSEIN ROUNAGHI*, MAHMOOD CHAMSAZ and
AZIZOLLAH NEZHADALI
Department of Chemistry, Ferdowsi University of Mashhad, Mashhad, Iran

Abstract. The complexation of Pb^{2+}, Tl^+ and Cd^{2+} cations by 18-crown-6 was studied in water/propanol (H_2O/PrOH), water/acetonitrile (H_2O/AN) and water/dimethylformamide (H_2O/DMF) binary systems at 20 °C using square wave polarography (SWP) and differential pulse polarography (DPP). It was confirmed that the stoichiometry of each of the complexes formed between 18C6 and the respective cations is 1 : 1. The formation constants of the complexes were found to increase with increasing concentration of the non-aqueous solvent. In all cases, a stability order of Pb^{2+} > Tl^+ > Cd^{2+} was observed. In general, the stabilities of individual complexes were found to decrease as the binary solvent mixture varied from H_2O/AN to H_2O/PrOH to H_2O/DMF.

Key words: 18-Crown-6, lead(II), thallium(I), cadmium(II), Mixed-solvent, Polarography

1. Introduction

Since Pedersen's first report on the synthesis and complexing properties of crown polyethers [1], a large number of investigations of the complexing abilities of these ligands has been reported and many new crowns have been synthesized [2]. The complexation of these ligands with a range of metal cations have been studied in both aqueous solution as well as in a variety of non-aqueous solvents [3–10]. Metal complexation reactions in mixed solvent systems have been investigated to a much more limited extent [4] and the available information on such reactions with metal cations in mixed solvents appears to be very sparse. In most studies of this type, one of the solvent components was water while the other was an organic solvent that served to increase the solubility of the complex [4]. The preparation of such solvent mixtures can be regarded as a dilution of the aqueous solution with a miscible organic solvent and, of course, this process results in a shift in the association-dissociation equilibria existing in solution.

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* Author for correspondence.

An aim of many studies involving complex formation in mixed solvent systems has been to investigate the effect of solvent composition on the stability and nature of the complexes formed. It is well known that the strength of complexation is normally strongly dependent on the solvating ability of the solvent with respect to the cation and the ligand. As a result, variations in the nature of the solvent has often been demonstrated to produce significant changes in the binding affinities of macrocyclic ligands as a consequence, the stability (and selectivity) associated with complex formation can be greatly altered [11].

Various physicochemical methods have been used to obtain the stability constants of complexes of cyclic polyether complexes [12–22]. Of the various techniques, polarography has proved to be a useful means for investigating both the stoichiometry and stability of such complexes.

It was of interest to us to investigate the effect that the relative cation and ligand cavity sizes, the nature of the cation, and the properties of the solvent system have on the selectivity and stability of 18C6 crown ether complexes incorporating the toxic heavy metal ions, Pb^{2+}, Tl^+ and Cd^{2+}. In the present work, we report a polarographic investigation of the complex formation between 18-crown- 6 and these metal cations in $H_2O/PrOH$, H_2O/AN and H_2O/DMF binary systems.

2. Experimental

2.1. REAGENTS AND SOLVENTS

Reagent grade 18-crown-6 (Riedel) and tetraethylammonium chloride (TEAC), lead(II) nitrate, thallium(I) nitrate and cadmium(II) nitrate (all from Merck) were used without further purification except for drying over P_2O_5 in a vacuum for 48 h. Acetonitrile (Merck), dimethylformamide (Merck) and *n*-propanol (Riedel) were of the highest purity available and triply-distilled water was used for the preparation of the respective mixed solvents.

2.2. APPARATUS

The polarographic measurements (DPP and SWP) were carried out on an EG and G Princeton Applied Research (PAR), 384B polarographic analyzer with a static mercury drop electrode (SMDE) in a three-electrode arrangement (EG and G PAR 303A). A Ag/AgCl electrode with a bridge containing the same electrolyte as the electrolysed solution was employed. The counter electrode was a Pt wire. A solution of 0.025 M tetraethylammonium chloride was used as the base electrolyte. All solutions were deaerated for 8 minutes with pure helium prior to measurement and an inert atmosphere was maintained over the solution during the measurement. The instrumental parameters were pulse height, 20 mV; equilibration time, 5 s; scan rate, 200 mV/s for the SWP technique. The usual drop step time, (0.6 s); scan rate 4 mV/s and pulse height, 20 mV were used for the DPP experiments.

3. Results and Discussion

The polarographic determination of metal complex formation constants was based on measurement of the shift in the half-wave potential ($E_{1/2}$) or the differential pulse peak potential (E_p) as the concentration of ligand in solution was varied [23].

The complexation of Pb^{2+}, Tl^+ and Cd^{2+} by 18C6 was studied in $H_2O/PrOH$, H_2O/AN and H_2O/DMF binary systems at 20 °C using SWP and DPP. The shift in half-wave (or peak) potential relative to the concentration of which ligand was present in excess in solution, was found to be in accordance with the Lingane equation [24]:

$$\Delta E_{1/2} = (E_{1/2})_C - (E_{1/2})_M = -(RT/nF)(\ln K_f + m\ln[L]_t, \tag{1}$$

where $(E_{1/2})_C$ and $(E_{1/2})_M$ are the half-wave potentials of the complexed and free metal ion, n is the number of electrons transferred, K_f is the formation constant of the complex, m is the stoichiometry of the complex and $[L]_t$ is the analytical concentration of the ligand. The values of m and K_f can be obtained from the slope and intercept of the linear plots of $\Delta E_{1/2}(TR/nF)$ vs $\log[L]_t$, respectively.

In general, in the binary mixed solvents employed, addition of ligand to the respective cation solutions in 0.025 M TEAC, shifts the reduction potential, E_p, of the metal ion towards a more negative value. Polarograms of the Pb^{2+} ion in the presence of different concentrations of 18C6 in H_2O/DMF binary systems are shown in Figure 1. Similar polarograms were obtained for the other systems investigated.

In general, the cyclic voltammetric results show that the reduction of Pb^{2+}, Tl^+ and Cd^{2+} in the presence of ligand is reversible. The variations in $\Delta E_{1/2}(RT/nF)$ as a function of $\log[18C6]_t$ (for complex formation between 18C6 and Pb^{2+} ion in H_2O/DMF) are shown in Figure 2. The slope of the linear plots gave a value of $m = 1$, in agreement with the formation of a 1:1 complex between Pb^{2+} ion and 18C6 in solution; similar behavior was observed for the other systems. The formation constants of compexes were obtained by fitting the polarographic data to Equation (1). The results are presented in Table I.

As is evident from Table I, in all three binary mixed solvents the metal complex stabilities for 18C6 decrease in the order $Pb^{2+} > Tl^+ > Cd^{2+}$. The Pb^{2+} ion, with its less soft character, and being a good fit for the cavity of 18C6 [25], forms the most stable complex (Figure 3). On the other hand, Cd^{2+} forms the least stable complex in the presence of TEAC (0.025 M). Previous results show that a relatively stable 18C6-Cd^{2+} complex is formed in the presence of perchlorate ion (tetraethylammonium perchlorate, TEAP, 0.025 M) in AN-H_2O mixed systems, reflecting the relatively strong affinity of Cd^{2+} for chloride ions [30]. Therefore, in some cases, the stability (selectivity) of complexes may change in the presence of different types of anion. As is evident from Table I, the stability constant for 18C6-Cd^{2+} decreases rapidly with increasing concentration of organic solvent. Since the

Table I. Log of the formation constants of 18C6-Pb^{2+}, 18C6-Tl$^+$ and 18C-Cd^{2+} complexes in binary aqueous/non-aqueous solvent mixtures, using SWP and DPP at 20 °C

Technique	Wt% of organic solvent in H$_2$O	Log K_f [a]		
		Pb^{2+} [b] $(r = 1.19\text{A})^c$	Tl$^+$ [b] $(r = 1.50\text{A})^c$	Cd^{2+} [b] $(r = 0.95\text{A})^c$
SWP	H$_2$O/PrOH			
	0	4.80	1.71	3.13
	16.67	5.17	1.12	<1
	34.78	5.80	1.31	<1
	54.54	I^d	2.24	<1
	76.19	I	2.12	I
DPP	H$_2$O/PrOH			
	0	4.55	<1	3.09
	16.67	4.89	1.2	<1
	34.78	5.97	1.32	<1
	54.54	I	2.40	<1
	76.19	I	2.18	I
SWP	H$_2$O/AN			
	0	4.80	1.71	3.13
	16.32	5.15	2.34	<1
	34.21	7.06	2.52	<1
	53.92	7.91	4.11	<1
	75.78	10.79	4.75	<1
SWP	H$_2$O/DMF			
	0	4.80	1.71	3.13
	19.19	4.50	–	<1
	38.76	4.35	1.78	<1
	58.76	3.96	2.50	<1
	79.17	2.26	3.06	<1
DPP	H$_2$O/DMF			
	0	4.55	<1	3.09
	19.19	4.13	–	<1
	38.76	4.41	1.15	<1
	58.76	3.77	1.77	<1
	79.17	2.04	1.86	<1

[a] Standard deviation = ± 0.09.
[b] The concentration of metal ions is 1.0×10^{-4} M.
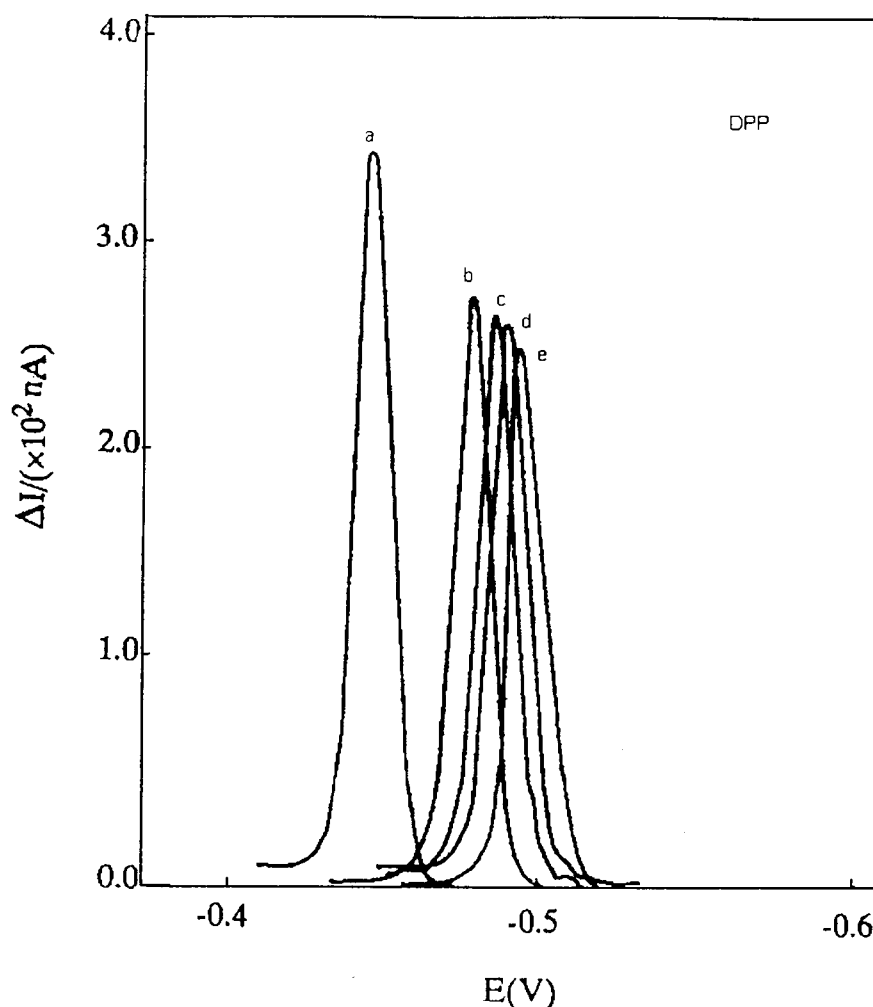[c] Ionic radius.
[d] I = Irreversible.

Figure 1. Differential pulse polarograms of 0.1 mM Pb^{2+} ion in H_2O/DMF (19.19% DMF + 81.81% H_2O binary system with different concentrations of 18C6 ligand: (a) 0.39, (b) 0.77, (c) 1.23, (d) 1.51 and (e) 1.91 mM.

concentration of chloride ion is high, this suggests that the stability of the chloro-complexes of Cd^{2+} may be strongly influenced by the nature of the organic solvent present in the binary mixture. In addition, it is known that *some* transition metal cations take part in binary complex and auto-complex formation [31]; and also in the formation of halogen bridged species in organic solvents with low or medium dielectric constant and donor number [33]. The formation of a weaker 18C6-Cd^{2+} complex with increasing amount of AN, PrOH and DMF in the binary mixtures, may also reflect such phenomena.

The data shown in Table I, as expected, generally show an increase in complex stability with increasing concentration of organic solvent in the mixed solvent
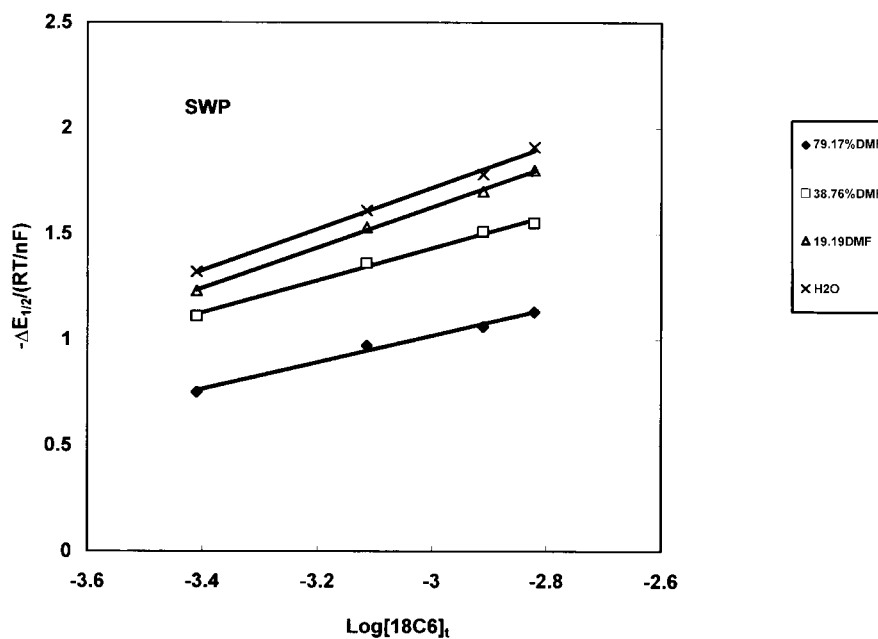
Figure 2. Linear plots of $\Delta E_{1/2}/(RT/nF)$ versus log $[18C6]_t$ for the 18C6-Pb^{2+} complex in H$_2$O/DMF binary mixtures.
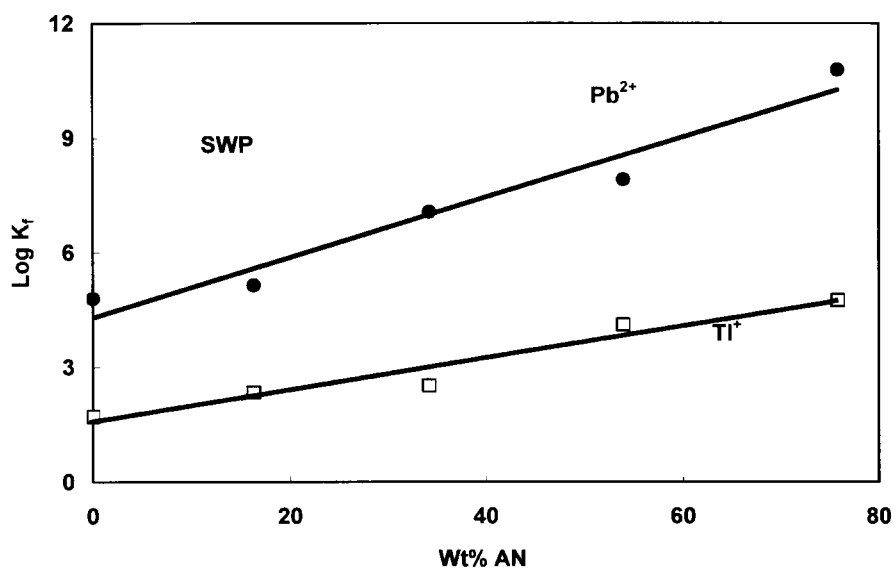

Figure 3. Variation of log K_f of complexes of 18C6 with Pb^{2+} and TI$^+$ ions in H$_2$O/AN binary systems.
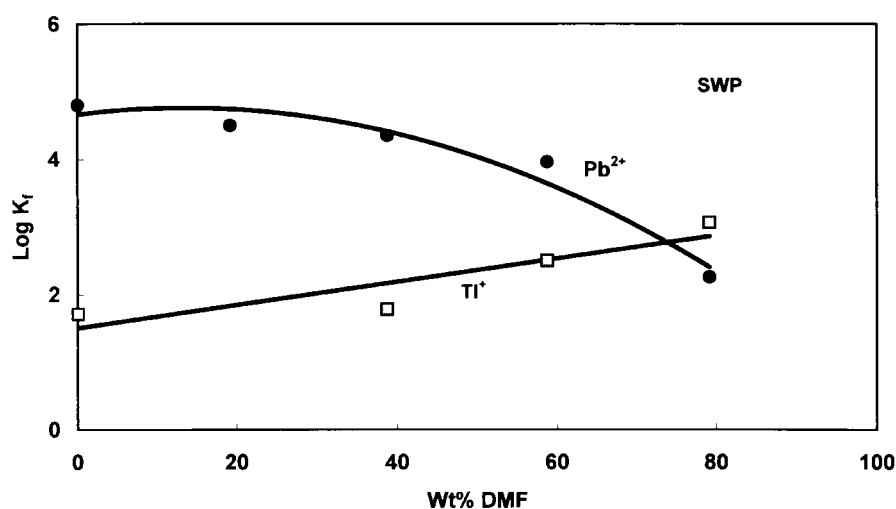
Figure 4. Variation of log K_f of complexes of 18C6 with Pb^{2+} and TI^+ ions in H_2O/DMF binary systems.

systems. The solvating ability of the solvent, as expressed by the Gutmann donicity scale, is useful for rationalizing such effects [19–22, 25–29]. That is, in a strongly solvating solvent such as water (DN = 33), 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), propanol (DN = 18) and dimethylformamide (DN = 26.6), the relatively poorer solvating ability of these solvents leads to an increase in the formation constant and this will also be the case when the concentration of these organic solvents is increased in binary mixed systems.

The variation in formation constants of the 18C6-Pb^{2+} and 18C6-Tl^+ complexes as a function of solvent composition in H_2O/DMF and H_2O/AN binary mixtures is shown in Figures 3 and 4. There is a linear relationship between the log K_f values and the weight percent of DMF and AN in the respective mixed solvent systems. It seems reasonable to assume that in most cases, it is the preferential hydration of the cations that is responsible for this monotonic dependence of stability constant on the solvent composition present.

Although the solvation of the cation is an important factor in complexation reactions, solvation of the ligand and resulting complex has also been well documented to contribute to the overall free energy for complex formation. The increased stability of 18-crown-6 cation complexes with increasing concentration of organic solvent has been claimed to arise from stabilization of the complex and destabilization of the free cation and crown ether in the presence of increased concentration of organic solvent [34]. As illustrated in Figure 4, for of Pb^{2+} complexation by 18C6, in spite of the lower donor ability of DMF relative to H_2O, the stability of 18C6-Pb^{2+} complex decreases with increasing concentration of DMF in H_2O/DMF

binary systems. In this case, the Pb^{2+} ion and anion may be more stabilized in DMF than in H_2O. Alternatively, the solvation of the complex may make a destabilizing contribution to complex formation on passing from water to dimethylformamide.

Inspection of the data in Table I shows that the formation constants obtained by differential pulse polarography and square wave polarography in most cases lie within experimental error. Finally, it is noted that due to the higher speed, higher resolution and also low consumption of mercury, SWP is the preferred technique for studies of the type presented in this report.

Acknowledgement

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