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Cyclic Voltammetric Study of the Complexation of Pb^{2+} Ions by Dibenzopyridino-18-crown-6 in Some Nitriles*

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A cyclic voltammetric study of the interaction of Pb^{2+} ions with dibenzopyridino-18-crown-6 in acetonitrile, propionitrile, butyronitrile, benzyl cyanide and benzonitrile has been carried out at various temperatures. Stability constants of the resulting 1:1 complexes were found to decrease with increasing DN, the solvent donor number. The enthalpy and entropy of complexation were calculated from the temperature dependence of the stability constants; the complexes were enthalpy stabilized, but entropy destabilized in all the solvents under study. The relationships ΔH^o *vs.* DN and ΔS^o *vs.* DN were found.

Key words: dibenzopyridino-18-crown-6, Pb^{2+} complexes, cyclic voltammetry, thermodynamics of complexation

Lead, which is extremely toxic and polluting agent, is still emited to the biosphere as a result of being use as the anti-knock additive to petrol and also due to its important applications in industry. In this situation, taking into account the problems of preconcentration and selective removal from various matrices, the study of complexes formed by macrocyclic compounds, *e.g.* crown ethers, with Pb^{2+} ions is of special interest [1]. Nevertheless, available information on such complexes in aprotic media is rather limited [2,3]. Moreover, a great part of studies have been carried out in binary solvent mixtures [4–10], and such state of knowledge stimulated us to undertake a more systematic investigation in pure dipolar aprotic liquids. As a consequence, we described previously thermodynamic aspects of the binding of Pb^{2+} with 18-crown-6, benzo-18-crown-6 and dibenzo-18-crown-6 in acetonitrile (MeCN), propionitrile (PrCN), propylene carbonate, *N,N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) [11].

It is well known that the replacement of oxygen atoms in crown ethers by sulfur and/or nitrogen atoms visibly affects the stability constants (K_S) of the complexes with a given cation [2,3]. The evaluation of pyridine nitrogen as a macrocyclic donor atom is desirable [12] and it has been shown that the ion selective electrode based on dibenzopyridino-18-crown-6 (DBPy18C6) revealed very good selectivity for Pb^{2+} over the variety of other cations in aqueous media [13]. A chloroform membrane

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* Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.

containing a DBPy18C6 carrier was found to be an excellent system for the uphill transport of Pb^{2+} [14]. Recently, the K_s values of Pb^{2+}–DBPy18C6 complexes have been determined in binary mixtures of MeOH, PrOH, $MeNO_2$ and MeCN with DMF [6]. Next, thermodynamic studies led to the conclusion that these complexes are enthalpy stabilized, but entropy destabilized in MeCN–DMSO systems [7], whereas both entropy and enthalpy stabilization was ascertained in methanol solutions [15].

In the present paper we report a cyclic voltammetric study of the complexation of Pb^{2+} with DBPy18C6 in some nitriles, namely in benzonitrile (PhCN), benzyl cyanide (BzCN), MeCN, PrCN and *n*-butyronitrile (BuCN), in order to investigate the stability and thermodynamic parameters of the resulting complexes.

EXPERIMENTAL

Crown ether DBPy18C6 from Merck was used without further purification except for vacuum drying over P_2O_5. Lead(II) perchlorate trihydrate (Aldrich) was vacuum dried (50°C) over P_2O_5. MeCN (Fluka) was purchased as the solvent certified for UV-spectroscopy and used without purification. All remaining solvents from Fluka vere dried over molecular sieves of 3A type and distilled under reduced pressure in argon atmosphere; the middle 50% fraction of the distillate was used in the experiments. Tetraethylammonium perchlorate (TEAP) from Merck was purified by recrystallization from triply distilled deionized water and vacuum drying. In typical experiments, concentrations of Pb^{2+} and TEAP were 0.5 mM and 0.1 M, respectively. Apparatus and all remaining experimental details were reported previously [11].

RESULTS AND DISCUSSION

Lead(II) ions when studied by cyclic voltammetry on a hanging mercury electrode undergo two-electron reduction to the metal amalgam in all the solvents under study

$$Pb^{2+} + 2\,e \leftrightarrows Pb(Hg) \qquad E^o \tag{1}$$

The limiting current in either case is controlled by mass transfer. Current – potential curves (scan rate 0.1 V s^{-1}) with equal peak currents in the cathodic and anodic sweeps and with $E_{pa} - E_{pc} = 30 \pm 3$ mV were obtained in all cases confirming the reversibility of reaction (1). Note that the E^o value was not influenced by varying concentration of supporting electrolyte (0.02–0.1 M), therefore it may be assumed as aproximately equal to the formal potential of the $Pb^{2+}/Pb(Hg)$ redox couple in a given medium. Addition of the ligand, DBPy18C6, shifts the E^o potential towards more negative values, while the reversibility of the electrochemical process is preserved as before. Thus the stoichiometry and stability constants of the resulting complexes can be examined by determining the E’ potentials in solutions of various ligand concentrations, C_L.

The plots of $\Delta E = E' - E^o$ against C_L were linear with slopes of 30 ± 4 mV/log C_L unit, and this finding may be taken as the evidence that the complexation is of 1:1 type in all the solvents being an object of our interest. Thus, the simple Lingane equation [16]

$$E^o - E' = (RT/2F)\ \ln(K_sC_L) \tag{2}$$

can be used to calculate the corresponding K_s values. Recall that the assumption made in deriving eq. (2) is that the ligand concentration is much larger than that of the metal ion. This condition was fullfilled in our experiments; the C_L values varied from 4 to about 70 mM. It is worth noting, furthermore, that in the calculations of stability constants, ion pairs formation between Pb^{2+} and the bulkly ClO_4^- anion was neglected under the highly diluted conditions. This is in accordance with the finding that the E^o values are independent of the concentration of TEAP. Table 1 summarizes the stability constants calculated according to eq. (2).

Table 1. Temperature effect on the stability constants of the Pb^{2+}–DBPy18C6 complex in various solvents.

Solvent	log K_s			
	22°C	30°C	40°C	50°C
PhCN	4.9_1	4.6_2	4.3_5	4.1_4
MeCN	4.5_5	4.3_2	4.0_8	3.9_3
BzCN	4.2_6	4.0_5	3.9_0	3.6_8
PrCN	4.0_3	3.8_5	3.6_7	3.5_3
BuCN	3.8_6	3.6_9	3.5_2	3.4_5

The data in Table 1 illustrate clearly the decisive influence of the solvent properties on the stability of the Pb^{2+}–DBPy18C6 complex. It has been shown many times that the solvating ability of a solvent, as expressed by DN, the Gutmann donor number, plays an important role in complexation of different cations with macrocyclic ligands; for more recent results see *e.g.* [11,17–19]. There is actually a linear relationship between log K_s and DN (Fig. 1). One can assume, therefore, that the

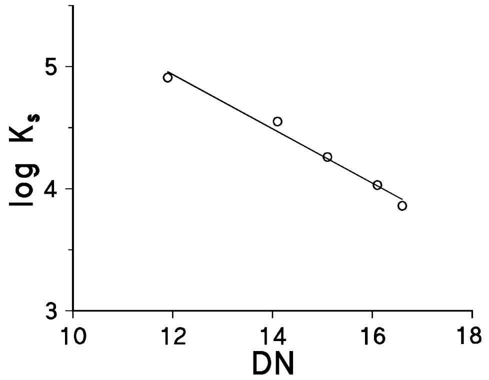

Figure 1. A plot of the log K_s values (22°C) for the Pb^{2+}–DBPy18C6 complex *vs.* the solvent donor number. Correlation coefficient of regression line is r = 0.9915.

solvent effect considered by us is restricted to the solvation of cationic species, particularly to the solvation of the free Pb^{2+} ions. Note also that the Pb^{2+} complex with DBPy18C6 revealed a visible increase in stability over the Pb^{2+}–DB18C6 one [11], at least in MeCN and PrCN solutions. Obviously, the last finding could be due to stronger interaction of the cation as a soft acid with the pyridine nitrogen atom of the DBPy18C6 ligand as a soft base, in comparison with the hard oxygen atoms of DB18C6.

In order to better understand the thermodynamics of complexation, it is useful to consider the enthalpic and entropic contributions to this process. The corresponding magnitudes of ΔH^o and ΔS^o were then evaluated by measuring the K_s values as a function of temperature (Table 1). The plots of $\log K_s$ *vs.* 1/T, according to the van't Hoff equation

$$2.303 \log K_s = -\Delta H^o/(RT) + \Delta S^o/R \tag{3}$$

were linear for all the solvents studied; the enthalpies and entropies were determined in the usual manner from the slopes and intercepts, respectively. From the data in Table 2 it is obvious that the formation of the Pb^{2+}–DBPy18C6 species is exoenthalpic.

Table 2. Thermodynamic parameters (± standard deviation) for the Pb^{2+}–DBPy18C6 complex in various solvents.

Solvent	$-\Delta H^o$, kJ mol^{-1}	$-\Delta S^o$, J mol^{-1} K^{-1}
PhCN	44 ± 2	54 ± 5
MeCN	36 ± 2	33 ± 6
BzCN	32 ± 3	26 ± 8
PrCN	28 ± 1	19 ± 4
BuCN	24 ± 2	7 ± 6

On the other hand, the entropic contribution disfavours the complex formation in all the solvents used in this investigation. It seems reasonable to assume that the terms that dominate the magnitude of ΔH^o are the interaction energies between the lead(II) cation and the ligand, as well as the solvation energies of free and complexed species. On the basis of Fig.1, the competition of the solvent molecule with the DBPy18C6 ligand for Pb^{2+} cations is expected to decrease with increasing solvent donicity. In other words, the diminution of the cation-ligand interaction would really result in little negative ΔH^o values. Next, the ΔS^o values depend on the number of reacting species, including the molecules involved in the solvation shell of the cation [20] and any conformational changes of the ligand upon complexation. One can assume, however, that the main justification for the negative sign of ΔS^o is the decrease in the conformational entropy brought about upon complexation from a flexible free ligand to a rigid complex [21–26]: as the cation-ligand binding becomes stronger, the degree of freedom of Pb^{2+}–DBPy18C6 is diminished, mainly because of the increased rigidity of the complex structure. Thus, the negative change in entropy cancel some of the enthalpic gain resulted from stronger binding. From the formal point of view, the rearrangement of solvent structure upon the conversion of a rather small solvated cation into a large complexed one, may contribute too. Such an effect was recognized in aqueous solutions [27], but it seems to be of secondary importance in nitriles, *i.e.* in much less structured liquids in comparison with water.

Finally, it is interesting to note that the ΔH^o and ΔS^o values are dependent on DN of the solvent as it is shown in Fig. 2. The following linear regressions were obtained by applying least-squares procedure:

$$\Delta H^o = 4.10\ (\pm 0.27)\ \mathrm{DN} - 93.32\ (\pm 3.94) \quad (4)$$

$$T\Delta S^o = 1.17\ (\pm 0.18)\ \mathrm{DN} - 26.74\ (\pm 1.77) \quad (5)$$

indicating that satisfactory co-linearity exists between ΔH^o and DN as well as between $T\Delta S^o$ and DN (here T = 295 K). The first of these holds with r = 0.9938 and with the value of the Fisher test of F = 239.2, whereas the second one is characterized by r = 0.9847 and F = 95.8. In our opinion this is the evidence that the compensating effect between ΔH^o and ΔS^o does exist in the systems under study. At present, however, it is too early to discuss quantitatively the problem of an extent of this compensation.

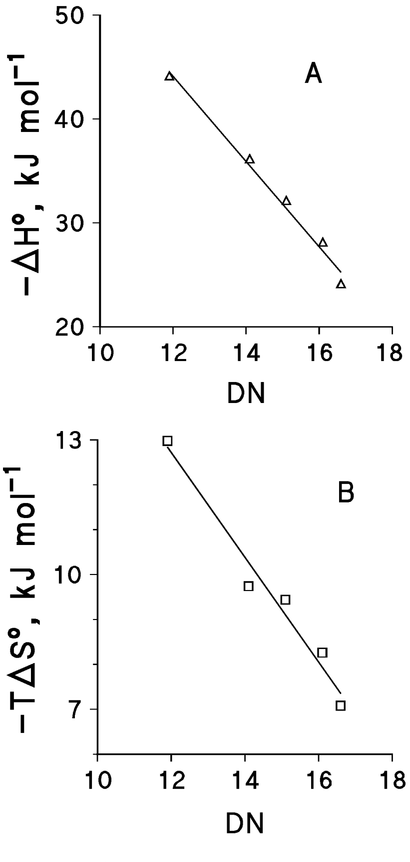

Figure 2. Plots of the ΔH^o (A) and $T\Delta S^o$ values (B) *vs*. the solvent donor number (T = 295 K).

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