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Differential Pulse Polarographic Study of Mercury Complexes with Some Benzo-Substituted Macrocyclic Diamides in Binary Nitromethane + Dimethylformamide Mixtures

by M. Shamsipur[1], A.R. Fakhari[2], H. Sharghi[3], H. Eshghi[4] and M.R. Ganjali[5*]

[1]*Department of Chemistry, Razi University, Kermanshah, Iran*
[2]*Department of Chemistry, Shahid Beheshti University, Tehran, Iran*
[3]*Department of Chemistry, Shiraz University, Shiraz, Iran*
[4]*Department of Chemistry, Sistan-Baloochestan University, Zahedan, Iran*
[5]*Department of Chemistry, Tehran University, Tehran P.O. Box 14155-6455, Iran*

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The complex formation of Hg^{2+} ion with five recently synthesized benzo-substituted macrocyclic diamides in binary nitromethane + dimethylformamide mixtures was studied by differential pulse polarography at 25°C. The stoichiometry and stability of the complexes were determined by monitoring the shift in the Hg^{2+} differential pulse peak potential against the macrocycles concentration. In all cases studied, it was found that the stability of the resulting 1:1 complex decreases drastically by increasing the amount of dimethylformamide in the binary mixtures. The observed stability order in a given solvent mixture is discussed in terms of the cavity size, structural flexibility and nature of the substituted on the macrocyclic diamide ring.

Key words: benzo-substituted macrocyclic diamide, mercury, polarography, mixed solvents

Since the first synthesis of macrocyclic crown ethers by Pedersen [1], study of these ligands and their metal ion complexes have received increasing attention [2,3]. By variation of ring parameters and structural units such as ring size, number and type of donor atoms and nature of substituted macrocyclic ligands, which can selectively bind cations, anions and even molecular compounds have been prepared [3,4]. It is well known that the substitution of some oxygen atoms of crown ethers by nitrogen or sulfur atoms drastically alter the complexing ability of the ligands towards different metal ions [2].

The design and synthesis of new functionalized macrocyclic ligands for specific analytical applications is a subject of continuous recent interest [5,6]. The in-built configuration rigidity induced by N-substituted amides present in the periphery of benzomacrocycles invokes pre-organization leading to ionophore selectivity [7,8]. A

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[*] Author for correspondence.

number of macrocyclic diamides have been shown to possess wide application in selective metal cation extraction [9,10].

We have recently reported the successful use of some benzo-substituted macrocyclic diamides in construction of Sr^{2+}, Zn^{2+} and Cu^{2+} PVC membrane sensors [11–13] and in polarographic study of mercury complexes in binary acetonitrile-water mixtures [8]. In this paper we report the differential pulse polarographic studies of mercury complexes with 1,13-diaza-2,3;11,12-dibenzo-4,7,10-trioxacyclopentadecane-14,15-dione (M_1), 1,13-diaza-2,3;11,12-dibenzo-4,7,10-trioxacycloheptadecane-14,17-dione (M_2), 1,13-diaza-2,3;11,12 -dibenzo-4,7,10-trioxacyclononadecane-14,19-dione (M_3), 1,13-diaza-2,3;11,12; 15,18-tribenzo-4,7,10-trioxacyclononadecane-14,19-dione (M_4) and 1,13 -diaza-2,3;11,12;15,17-tribenzo-4,7,10-trioxacyclooctadecane-14,18-dione (M_5) in binary nitromethane-dimethylformamide mixtures (see Fig. 1).

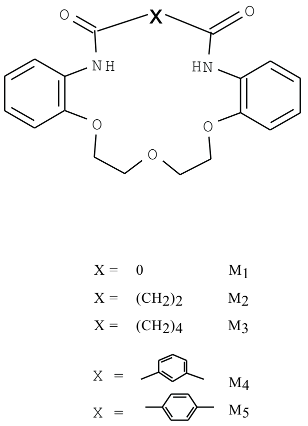

Figure 1. Structures of benzo-substituted macrocyclic diamides used.

EXPERIMENTAL

Reagents grade tetrabutylammonium perchlorate (TEAP, Merck) was used without any further purification except for vacuum drying over P_2O_5. HPLC grade nitromethane (NM) and dimethylformamide (DMF) (both from Fluka) were used to prepare the solvent mixtures by weight. M_1, M_2, M_3, M_4 and M_5 were synthesized, purified and dried as described elsewhere before [7].

The polarographic measurements were carried out with a dropping mercury electrode (DME) in a three-electrode arrangement. The counter electrode was a platinum wire with a considerably larger surface area than that of the DME. A silver | silver chloride | saturated KCl reference electrode was placed in a 0.1 M TEAP solution in non-aqueous solvents (DMF + NM mixture) connected to the electrolyzed solution by means of a bridge containing the base electrolyte. All the solutions were deaerated for 10 min with pure argon and an inert atmosphere was maintained over the solution during the oxidation. A Polarecord E-506 Metrohm Herisau instrument was used for the polarographic measurements. The usual instrumental parameters were: constant drop time, 0.8 s; mercury height, 50 cm; scan rate, 5 mV s^{-1}; pulse duration, 0.02 s; pulse magnitude, 40 mV. All experiments were carried out at 25 ± 0.1°C using a model FK2 Haake thermostat with water bath.

The determination of the stability constants of Hg^{2+}-crown ether complexes, studied in different solvents, was based on measurements of the half-wave potentials $E_{1/2}$ brought about by the addition of an increasing amount of the ligands [14]. In all experiments the concentration of TEAP, as supporting electrolyte, was kept constant at 0.025 M and the concentration range of the macrocyclic ligands added was 1.0×10^{-3} to 10^{-2} M.

It is well known that mercury from the DME can be oxidized anodically to its bivalent state leading to the overall electrode process [15].

$$Hg = Hg^{2+} + 2e^{-} \tag{1}$$

In the presence of most complexing agents, this oxidation reaction can be facilitated by chemical complexation following the electrochemical oxidation of mercury [15].

$$Hg + pL = [HgL_p]^{2+} + 2\ e^{-} \tag{2}$$

The half-wave potential $E_{1/2}$ of this process is related to the ligand concentration [L] and the stability constant β_p, by the well-known equation [14]

$$E_{1/2} = E^{o}_{Hg} + \frac{RT}{2F}\ln\frac{2^{(p-1)}D^{1/2}}{p(D')^{1/2}\beta_p[L]^{(p-1)}} \tag{3}$$

where D and D' are the diffusion coefficients of the ligand and complex in solution respectively; the ratio of these two values is reasonably assumed to be unity [14]. It has been reported that the peak potential E_p in differential pulse polarography is related to the half-wave potential $E_{1/2}$ of the corresponding d.c. polarogram by the expression [16] $E_p = E_{1/2} - \Delta E/2$, where ΔE is the magnitude of the differential pulse. In cases where ΔE is small, E_p lies very close to the value of $E_{1/2}$ [17]. It is clear that E_p and $E_{1/2}$ are linearly related and thus it is possible to replace $E_{1/2}$ with E_p in (3). The free ligand concentration [L] in equilibrium with Hg^{2+} depends on the total concentration C_L of ligand and pH according to the equation

$$[L] = C_L/a_{L(H)} \tag{4}$$

where $a_{L(H)}$ is the proton side reaction coefficient. Considering the fact that $E_p \approx E_{1/2}$, substitution of [L] from (4) into (3) and rearrangement gives:

$$E_p = E^{o}_{Hg} - \frac{RT}{2F}\ln\beta_p - \frac{RT}{2F}\ln c_L^{(p-1)} + \frac{RT}{2F}\ln\frac{2^{(p-1)}}{p}\alpha_{L(H)}^{(p-1)} \tag{5}$$

In the mixed solvents used there is no proton side reaction and $\alpha_{L(H)}$ can be taken as unity, Thus, (5) can be simplified to:

$$E_p = E^{o}_{Hg} - \frac{RT}{2F}\ln\beta_p - \frac{RT}{2F}\ln c_L^{(p-1)} + \frac{RT}{2F}\ln\frac{2^{(p-1)}}{p} \tag{6}$$

where E^{o}_{Hg} is the formal potential of the Hg^{2+}/Hg couple. The reported value for E^{o}_{Hg} in aqueous solution is 0.589 V *vs.* SCE at an ionic strength of 1.0 M [18]. Unfortunately, reports on E^{o}_{Hg} in mixed and non-aqueous solutions are quite sparse [19]. But, as in aqueous solution, the formal potentials should be very close to the mercury electrode potentials. Therefore, in the mixed solvents used in this study, the oxidation potentials of the mercury electrode were used for E^{o}_{Hg} in (6) [20]. The oxidation potentials of the mercury electrode in the nitromethane + dimethylformide mixtures used were obtained from the intersection of the anodic pulse polarograms of the corresponding 0.025 M TEAP solutions in the absence of any ligand with their base lines. Errors associated with the potentials were reported as ±SD from at least three replicate measurements. However, it should be noted that, owing to some differences in the properties of various solvents used, the existence of some different contributions from possible liquid junction potentials (although at a low relative level) to be measured E°_{Hg} values cannot be neglected.

RESULTS AND DISCUSSION

In all five nitromethane + dimethylformamide mixtures used, the electrochemical process for the oxidation of mercury electrode was reversible and diffusion controlled. As an example, the anodic differential pulse polarograms of the mercury electrode in the presence of ligand M_2 in different solvent mixtures are shown in Fig. 2. It is interesting to note that, in all cases studied, the peak potentials for electrochemical oxidation of mercury in the presence of different macrocyclic diamides were found to be independent of the ligand concentration, while only an increase in the peak current was observed with increasing ligand concentration. This behavior, which is in accordance with P = 1 in (6), indicates the formation of 1:1 complexes of Hg^{2+} with the ligands in solutions.

The E_{appl} *vs*. log $[I/(I_d - I)]$ for the corresponding dc polarograms gave straight lines of Nernstian slope corresponding to a reversible two-electron oxidation (30 ± 2 mV). The observation of relatively narrow differential pulse peaks in all cases studied further supports the reversible behavior of the Hg°/Hg^{2+} couple [16]. This reversible behavior indicates that the exchange between the Hg^{2+}-crown species is rapid on the measurement time scale.

The anodic oxidation potentials of the mercury electrode in various solvent mixtures were measured and are given in Table 1. It is interesting to note that there is a relative good linear correlation between the oxidation potential of mercury and the molar fraction X_w of DMF in the mixed solvent. The higher the molar fraction of DMF, the easier is the oxidation and dissolution of Hg° in the solution.

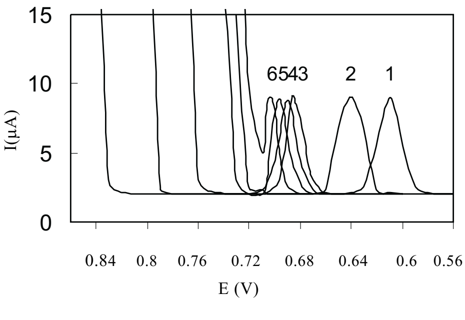

Figure 2. Anodic differential pulse polarograms of mercury electrode in 0.025 M TEAP in different nitromethane-dimethylformamide mixtures in the presence of 5×10^{-3} M of ligand M_2 at 25°C W% of nitromethane in the solvent mixtures is: 1 (100%), 2 (90%), 3 (80%), 4 (70%), 5 (60%), 6 (50%).

Table 1. Oxidation potentials of mercury electrode in nitromethane and different nitromethane + dimethylformamide mixtures containing 0.025 M TEAP at 25°C

Solvent composition (wt% of DMF in NM)	Potential/mV
0	860 ± 10
10	830 ± 10
20	795 ± 10
30	754 ± 10
40	746 ± 10
50	739 ± 10

The formation constants of the resulting 1:1 complexes were determined from the following simplified equation by the measurement of E_p and E°_{Hg} in the presence and absence of ligands, respectively:

$$E_p - E^{\circ}_{Hg} = -(RT/2F)\ln\beta_1 \qquad (7)$$

Since E_p and E°_{Hg} are measured under the same experimental conditions, except for the presence of neutral crown ethers in the case of E_p, the effects of possible liquid junction potentials would cancel out in (7).

All calculated formation constants for the resulting 1:1 complexes between Hg^{2+} ion and ligands M_1–M_5 in different nitromethane + dimethylformamide mixtures at 25°C are summarized in Table 2. It is immediately obvious that the solvent properties have a very fundamental effect on the stability and selectivity of the resulting complexes. In all cases, the stability of the complexes decreases drastically with increasing weight percent of dimethylformamide in the mixed solvent. It has been shown that the solvating ability of the solvent, as expressed by the Gutmann donicity number [21], plays an important role in the complexation reactions [3,22,23].

Table 2. Stability constants of Hg^{2+} complexes with different benzo-substituted macrocyclic diamides in nitromethane and nitromethane + dimethylformamide mixtures at 25°C.

Ligand	Logβ$_1$					
Solvent composition wt% of dimethylformamide in nitromethane	0	10	20	30	40	50
M_1	8.20±0.1	6.24±0.1	3.58±0.07	2.00±0.07	< 2	< 2
M_2	8.62±0.1	6.62±0.1	4.00±0.05	1.09±0.12	1.09±0.12	< 2
M_3	7.62±007	5.89±0.1	3.24±0.07	1.53±0.1	< 2	< 2
M_4	6.96±0.05	5.11±0.07	2.93±0.1	< 2	< 2	< 2
M_5	6.42±0.05	4.44±0.07	2.5±0.1	< 2	< 2	< 2

Dimethylformamide is a solvent of high solvating ability (DN = 26.6) [24], which can compete strongly with the ligands for Hg^{2+} ion. Thus, it is not surprising that the addition of dimethylformamide to nitromethane as a low donicity solvent (DN = 2.7) [24] will decrease the extent of interaction between the ligand donating atoms and Hg^{2+} ion.

It is interesting to note that, in all cases studied, there is actually a linear relationship between $\log\beta_1$ and the mole fraction X_{DMF} of dimethylformamide in the mixed solvents. The same trend has already been reported for a variety of complexes in different solvent mixtures [8,25].

From Table 2 it can be seen that the stability of the resulting 1:1 complexes of Hg^{2+} ion with different macrocyclic diamides decreases in the order $M_2 > M_1 > M_3 > M_4 > M_5$. There are at least three factors which can make significant contributions to the stability of the metal ion complexes with benzo-substituted macrocyclic diamides: (1) The cavity size-cation diameter ratio, (2) the nature of substituents on the macrocyclic ring, (3) the conformations of the free and complexed macrocyclic ligands.

As can be seen from Fig. 1, the total number of ring atoms in the benzo-substituted macrocylic diamides used is 15 for M_1, 17 for M_2, 18 for M_4 and 19 for M_3 and M_5. The Hg^{2+} ion with an ionic radius of 1.19 Å [26] seems to have the best fitting condition inside the 17 membered crown used (M_2), resulting the most stable complexes in the series. On the other hand, the macrocycles M_1 and M_3 with smaller (15-membered) and larger (19-membered) cavity sizes respectively, form mercury complexes of lower stability.

The substitution of a third benzo group in the structure of macrocycles M_4 and M_5 will result in diminished complexing ability of these ligands, so that the resulting Hg^{2+} in complexes are the least stable in the series. This is due to a combination of the decreased donating ability of the macrocycles diamide group, related to the electron withdrawing effect of the benzo group, and reduced flexibility of the macrocyclic rings. However, some higher stability of the mercury complex with M_4 over that of M_5 is most possibly due to a better fitting condition of former ligand for Hg^{2+} ion.

REFERENCES

1. Pedersen C.J., *J. Am. Chem. Soc.*, **89**, 7017 (1967).
2. Izatt R.M., Bradshaw J.S., Nielsen S.A., Lamb J.D., Christensen J.J. and Sen D., *Chem. Rev.*, **85**, 271 (1985).
3. Izatt R.M., Pawlak K., Bradshaw J.S. and Bruening R.L., *Chem. Rev.*, **91**, 1721 (1991).
4. Izatt R.M., Bradshaw J.S., Pawlak K., Bruening R.L. and Tarbet B.J., *Chem. Rev.*, **92**, 1261 (1992).
5. An H.Y., Bradshaw J.S. and Izatt R.M., *Chem. Rev.*, **92**, 543 (1992).
6. Gibson H.W. and Nagvekar D.S., *Can. J. Chem.*, **75**, 1375 (1997).
7. Sharghi H. and Eshghi H., *Tetrahedron,* **51,** 913 (1995).
8. Ganjali M.R., Eshghi H., Sharghi H. and Shamsipur M., *J. Electroanal. Chem.*, **405**, 177 (1996).
9. Paredes R.S., Valera N.S. and Lindoy L.F., *Aust. J. Chem.*, **39**, 1071 (1986).
10. Adam K.R., Leong A.J. and Lindoy L.F., *J. Chem. Soc. Dalton Trans.,* 1733 (1988).
11. Shamsipur M., Rouhani S., Sharghi H., Ganjali M.R. and Eshghi H., *Anal. Chem.*, **71**, 4938 (1999).

12. Shamsipur M., Rouhani S., Ganjali M.R., Sharghi H. and Eshghi H., *Sens. Actuators B*., **59**, 30 (1999).
13. Shamsipur M., Rouhani S., Ganjali M.R., Eshghi H. and Sharghi H., *Microchem. J*., **63**, 202 (1999).
14. Crow D.R., Polarography of Metal Complexes. Academic Press, NY, 1969.
15. Kolthoff I.M. and Miller C.S., *J. Am. Chem. Soc*., **63**, 1405 (1941).
16. Parry E.P. and Osteryoung R.A., *Anal. Chem*., **37**, 1634 (1965).
17. Bard A.J. and Faulkner L.R., Electrochemical Methods. Fundamentals and Applications, Wiley and Sons, NY, 1986.
18. Nyman C.J. and Parry E.P., *Anal. Chem*., **30**, 1255 (1958).
19. Wrona P.K. and Galus Z., Encyclopedia of Electrochemistry of the Elements, Vol. IX, A.J. Bard, ed., Dekker, NY, 1982.
20. Hojo M., Hajiwara M., Nagai H. and Imai Y., *J. Electroanal*. Chem., **234**, 251 (1987).
21. Gutmann V., Coordination Chemistry in Non-aqueous Solution, Springer Verlag, NY, 1960.
22. Hofmanova A., Koryta J., Brezina M. and Mittal L., *Inorg. Chim. Acta*, **28**, 73 (1978).
23. Yee E.L., Tabib J. and Weaver M.J., *J. Electroanal. Chem*., **96**, 241 (1979).
24. Gutmann V., The Donor – Acceptor Concept of Molecular Interaction, Plenum, NY, 1978.
25. Shamsipur M. and Ghasemi J., *J. Inclus. Phenom*., **28**, 315 (1997).
26. Shannon R.D., *Acta Cryst*., **32A**, 751 (1976).