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Electrochemical Studies of Tl(I) Crown-Ether Complexes in Nonaqueous Media

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Summary. Complexation equilibria of the Tl(I) ion with 18-crown-6 and dibenzo-18-crown-6 were studied polarographically in 10 nonaqueous solvents. The stability of the complexes is strongly influenced by the nature of solvents and varies with their Lewis basicities. It has been found that the log K_s value (K_s is the stability constant of the complex) can be well described by empirical relation log $K_s = a\,DN + b$, where DN stands for the Gutmann donor number and a and b mark the regression coefficient. Addition of the second explanatory parameter, the acceptor number, is not statistically significant. This result is in agreement with the predominant role of Tl(I) ion solvation.

Keywords. Solvent effect; Crown ether complexes; Donor number.

Elektrochemische Untersuchungen von Tl(I)-Kronenetherkomplexen in nichtwäßrigen Medien

Zusammenfassung. Es wurden die Komplexierungsgleichgewichte des Tl(I)-Ions mit 18-Krone-6 und Dibenzo-18-krone-6 polarographisch in 10 nichtwäßrigen Lösungsmitteln untersucht. Die Stabilität der Komplexe wird sehr stark vom Solvens beeinflußt, wobei eine starke Abhängigkeit von der Lewis-Basizität beobachtet wird. Es wurde festgestellt, daß die logK_s-Werte (K_s ist die Komplexstabilitätskonstante) gut mit der empirischen Beziehung log $K_s = a\,DN + b$ beschrieben werden können, wobei DN die Gutmann'sche Donorzahl und a und b die Regressionskonstanten bedeuten. Hinzunahme der Akzeptorzahl als zweiten Parameter bleibt statistisch insignifikant. Dieses Ergebnis stimmt mit dem dominierenden Einfluß der Tl(I)-Ionensolvatation überein.

Introduction

The stability of crown-ether complexes depends on several molecular factors; these include cavity size of the ligand, the character of the heteroatoms and spatial distribution of ring binding sites, the possible presence of substituents as well as the cation diameter [1–3]. One of the major factors is also the type of solvent used. The parameters governing substituting a solvent S, for water W, for M^+-*crown* interaction follows from the thermodynamic cycle [1].

$$\begin{tikzcd}[column sep=small]
M_w^+ \arrow[d] & + & crown_w \arrow[d] & \overset{K_w}{\rightleftharpoons} & (M^+\text{-}crown)_w \arrow[d] \\
M_s^+ & + & crown_s & \overset{K_s}{\rightleftharpoons} & (M^+\text{-}crown)_s .
\end{tikzcd} \qquad (1)$$

Accordingly, the stability constants are related through the free energy transfer terms, i.e.

$$-RT\ln(K_s/K_w) = \Delta G^0_{tr}(M^+\text{-}crown) - \Delta G^0_{tr}(M^+) - \Delta G^0_{tr}(crown). \qquad (2)$$

It is then clear that considering the solvent effects on the equilibrium constant, the free energies of transfer for the cations, for the complexed cations, and for the ligands should be taken into account.

On the other hand, however, it seems to be evident that among the terms participating in Eq. (2) $\Delta G^0_{tr}(M^+)$ is the chief contributor to the $\ln(K_s/K_w)$ value. This is a reason why effects of solvents on binding constants are most often discussed in connection with the energetics of cation solvation. Generally, two alternative but complementary viewpoints on the essence of solvation phenomena have been established.

According to the first, the solvent is considered as homogeneous, isotropic continuum which surrounds the molecules and/or ions of the solute. The intensity of solvent-solute interaction in solvents of this type is considered to be determined by macroscopic parameters of the solvent, e.g. electric permittivity, and the molecular/ionic characteristics of the solute. Solvent effects of this type caused by long-range force are assumed as non-specific universal interactions.

According to the second model, the medium should be characterized as anisotropic, and this feature determines the nature of the solvent-solute interactions. It is believed that such interactions are of chemical nature, i.e. short range and consisting of the formation of solvation complexes through donor-acceptor bonds which are localized in space in a definite manner. Solvent effect of this type are known as specific solvation effects. It should be emphasized that developments in various areas of chemistry have been decisively influenced by the ideas of the donor-acceptor concept.

It is noteworthy that both these models have been applied to interpret the solvent effects on the stability constants of Tl(I) macrocyclic complexes in non-aqueous media. Exemplarily, it is evident that, in general, the thallium complexes of crown-ethers with 18-atom cavities are quite stable in solvents of low donicities and the stability decreases with increasing the donor ability of a solvent [4]. Alternatively, an approximate linearity was found to exist between log K_s and the Kirkwood dielectric function for Tl(I)-benzo-15-crown-5 complex in alcohols [5], i.e. in solvents characterized by approximately the same Lewis basicities. In both two cases the solvent change of the log K_s values have been treated as limited by the ΔG^0_{solv} terms of ionic species, viz. $\Delta G^0_{solv}(\mathrm{Tl}^+)$ and $\Delta G^0_{solv}(\mathrm{Tl}^+\text{-}crown)$. The aim of this paper is to analyse how the Lewis basicity, and, possibly, the Lewis acidity of solvents may be used to explain and predict their effect on the complexation equilibria. To this purpose the reactions of the thallium(I) ion with 18-crown-6 (18 C 6) and dibenzo-18-crown-6 (DB 18 C 6) were studied in non proton-donating media.

Materials and Methods

Polarographic and cyclic voltammetric curves were determined in a three-electrode system, a Radelkis OH 105 apparatus being used. The potentials were measured against an aqueous SCE. Tetrabutylammonium perchlorate (0.05 *M*) was used as supporting electrolyte.

Benzonitrile (*BN*), acetonitrile (*ACN*), porpylene carbonate (*PC*), acetone (*AC*), sulfolane (*TMS*), N,N-dimethylformamide (*DMF*), N,N-dimethylacetamide (*DMA*), N-methyl pyrolidinone (*NMP*), dimethylsulfoxide (*DMSO*), and hexamethylphosphoramide (*HMPA*) were dried as described in [6] and fractionally distilled at reduced pressure under an argon atmosphere immediately prior to use. The crown ether 18C6 was purified by converting it to the acetonitrile complex and driving of acetonitrile under vacuum [7]; DB18C6 was recrystallized from benzene. Thallium(I) perchlorate (K & K) of AR-grade quality was dried at 120 °C.

The measurements were performed at a temperature of 23 ± 0.1 °C (in *TMS* at 30 ± 0.2 °C). All remaining experimental details have previously been described [5].

Results and Discussion

Among the differnet methods used for the investigation of metal complexes, polarography is undoubtedly unique owing to methodical simplicity and sufficient precision of the measurements. By the application of this technique, it is possible to determine the stability constants, the composition and the degree of formation of various metal-ligand systems in different media. Several mathematical models are advanced from time to time for their determination and can be found in review articles [8, 9] and monographs [9, 10]. This is a reason for which we have decided to employ polarographic measurements in our experiments.

Before we proceed with the interpretation of our results, some questions need to be answered. The first of these is connected with the fact that the electric permittivities of the solvents used are quite elevated, so we can neglect a possible competition from ion pair formation in $Tl^+ - ClO_4^-$ system. In reality, $TlClO_4$ is completely dissociated in *DMF* [12], while the ion association constant value in *ACN* was found to be 32 [13]. We assume, however, that such association does not influence significantly the complexation equilibria, because dilute solutions of $TlClO_4$ were used in our experiments.

Second, thallium(I) reduces at a dropping mercury electrode forming a single diffusion controlled wave in all he solvents under investigation. The shapes of the polarographic and cyclic voltammetric curves are in agreement with those characteristics for reversible one electron transfer. Thus, the half-wave potential of the electrochemical process

$$Tl^+ + e \rightleftharpoons Tl(Hg) \qquad (3)$$

may be assumed as approximately equal to the formal potential $E^0_{1/2}$ of the Tl(I)/Tl (Hg) redox system. The values of $E^0_{1/2}$ are collected in Table 1.

Third, addition of 18C6 and DB18C6, respectively, shifts the $E^0_{1/2}$ values in a negative direction, while the reversibility of the electrode process is preserved as before. So, the variation of the half-wave potential with the crown concentration (c_{crown}) can be used to calculate the equilibrium constant, K_s. In the case of 1 : 1 complexation the observed potential shift is given by [14]

$$\Delta E_{1/2} = E_{1/2} - E^0_{1/2} = (RT/F)\ln(K_s c_{crown}) + (RT/F)\ln(i_{Tl^+\text{-}crown}/i_{Tl^+}), \qquad (4)$$

where $E_{1/2}$ stands for the potential determined at a given c_{crown} value, whereas the ratio of limiting currents $c_{Tl^+\text{-}crown}/c_{Tl^+}$ corresponds to a change in the diffusion coefficient of Tl^+ upon complexation. Eq. (4) was derived assuming that c_{crown} is much larger than the concentration of the Tl(I) ions. As it can be seen from Table 2 this condition has been fulfilled in our experiments. Moreover, Eq. (4) indicates

Table 1. $E^0_{1/2}$ values of Eq. (4) for the polarographic reduction of the thallium(I) ion

No.	Solvent	*DN*	*AN*	$-E^0_{1/2}$ (mV)
1.	*BN*	11.9	15.5	166
2.	*ACN*	14.1	18.9	273
3.	*TMS*	14.8	19.2	415
4.	*PC*	15.1	18.3	242
5.	*AC*	17.0	12.5	238
6.	*DMF*	26.6	16.0	450
7.	*NMP*	27.3	13.3	458
8.	*DMA*	27.8	13.6	445
9.	*DMSO*	29.8	19.3	535
10.	*HMPA*	38.8	10.6	487

that for the 1 : 1 complex the half-wave potential should be linearly changed with log c_{crown} and $\Delta\Delta E_{1/2}/\Delta \log c_{crown} = 59\,\mathrm{mV}$. In reality, the last mentioned parameter was found to be $60 \pm 4\,\mathrm{mV}$ in all the solvents under study, so only 1 : 1 complexes were identified. For example, in *AC* solutions $\Delta\Delta E_{1/2}/\Delta \log c_{crown} = 60$ and 62 mV for 18C6 and DB18C6, respectively. In this same solvent Popov et al. [4] have reported the formation of 1 : 1 and 2 : 1 Tl(I)-DB18C6 complexes, but this divergence seems to be simply connected with different $c_{\mathrm{DB18C6}}/c_{\mathrm{Tl^+}}$ molar ratios.

Table 2 summarizes the stability constants calculated according to Eq. (4). It should be pointed out that most of the already published results for the ligand 18C6 in *TMS* [4], *DMF* [4], and *HMPA* [4] and for DB18C6 in *ACN* [15], *PC* [16, 17], *TMS* [4], and *DMF* [4] agree well with these values. As it can be seen, in a given solvent the complexing ability of 18C6 is greater than that of the DB18C6 ligand. Taking into account that the cavity size remained nearly the same, this observation may be elucidated by the difference in the electron density distribution at the binding sites [18]. It is also evident that the stability of the complexes is strongly influenced by the nature of the solvents. Therefore it was of interest to study whether the K_s values can be correlated with solvent characteristics.

We noted earlier that the interactions between the solvent and the solute are usually discussed in terms of specific and non-specific effects. In real systems, the effect of the solvent on a given physiochemical quantity may be more complicated. Generally, it is not easy to recognize the property of the solvent which has predominant influence on the quantity being an object of our interest; in many cases, the combined effect of a number of properties may appear. It means that single-parameter correlations are not universal.

A rigorous approach for solvent-solute interactions has been suggested by Koppel and Palm who argued that a complete description must include both non-specific and specific effects. They proposed [19] the general four-parameter equation which relates the variation of a given property to two non-specific and two specific characteristics of the solvent. The non-specific parameters measure polarization and polarizability, respectively, according to classical dielectric theory. Con-

Table 2. Stability constants, K_s (dm^3 mol^{-1}), for 18-crown-6,Tl$^+$ and dibenzo-18-crown-6,Tl$^+$ complexes. Concentration of thallium(I) ion, $c_{Tl(I)}$ was 0.03 *mM*. Errors in determination of K_s do not exceed ±20%

Solvent	18C6		DB18C6	
	c_{crown} (*mM*)	log K_s	c_{crown} (*mM*)	log K_s
BN	0.6–15	5.6	1.0–18	5.30
ACN	1.0–25	5.00	2.5–35	4.80
TMS	0.8–15	4.45	0.7–20	4.10
PC	1.5–18	5.10	2.0–26	4.92
AC	1.0–20	4.90	0.8–22	4.60
DMF	3.0–40	3.42	1.5–35	1.96
NMP	0.8–15	3.50	1.0–18	2.00
DMA	2.0–25	3.50	1.7–33	2.06
DMSO	1.2–22	1.88	1.5–30	0.78
HMPA	1.3–18	1.30	0.9–22	–

sequently, electric permittivity, ε, is the base of the first parameter and was used in the form of the Kirkwood function.

The function of the refractive index was used for the polarizability parameter. Next, two specific characteristics correspond to the Lewis basicity and the Lewis acidity of the solvent.

It seems to be evident, however, that for solvents with $\varepsilon > 20$ (this condition was fulfilled in our experiments) it is hopeless to expect any considerable contribution from non-specific interactions [20]. Hence, it was postulated that the solvent effect on a given physicochemical quantity can be represented as a planar function of two independent but complementary parameters being Lewis acidity and basicity parameters [21]. Unfortunately, at this time, there is no unambiguous way to measure these solvent properties. A number of empirical parameters have been introduced; a recent review is given by Reichardt [22]. Depite criticism of either the concept [23–25] or the experimental values [25–28], the donor number [29, 30], *DN*, is one of the most widely used empirical parameter of solvent basicity, particularly in the field of coordination chemistry. Moreover, it should be pointed out in this place, that cation solvation in different aprotic solvents may be successfully characterized by the donor numbers, e.g. a linear relationship exist between the latter and the chemical shift of the ^{205}Tl(I) nucleus in solutions in various solvents [31]. So, we chose the Gutmann donor number as a measure of solvent basicity. Of the various Lewis acidity parameters the acceptor number [30, 32], *AN*, was used. Thus, it is assumed that the solvent effect on K_s should be described in terms of the planar regression [21] in the following form,

$$\log K_s = a\,DN + b\,AN + c\,, \qquad (5)$$

where a and b are coefficients describing the sensitivity of K_s to basic and acidic solvent properties.

We shall now discuss our experimental results. First, using the data presented in Table 2, we obtained the single parameter regressions shown in Eqs. (6) and (7) for complexation of the Tl(I) ions by 18 C C 6 and DB 18 C 6, respectively,

$$\log K_s = -(0.153 \pm 0.017)\, DN + (7.276 \pm 0.394)\,, \qquad (6)$$

$$\log K_s = -(0.228 \pm 0.018)\, DN + (8.073 \pm 0.400) \qquad (7)$$

(errors are standard deviations).

The correlation coefficients were found to be 0.9564 and 0.9777, respectively. Then, satisfactory linear relationships exist between log K_s and DN in both cases under study (Figs. 1 and 2).

It is not surprising since log K_s values for various crown ethers and different metal ions were found to change inversely with DN [4, 33, 34]. However, the number of stability constants that had been determined was too small for the computation of a reliable correlation equation.

Next, the planar regressions including both the Lewis basicity and acidity parameters have been considered. Consequently, we have found (8) and (9) for the same set of experimental data used to calculate Eqs. (6) and (7),

$$\log K_s = -(0.174 \pm 0.014)\, DN - (0.115 \pm 0.039)\, AN + (9.560 \pm 0.830)\,, \qquad (8)$$

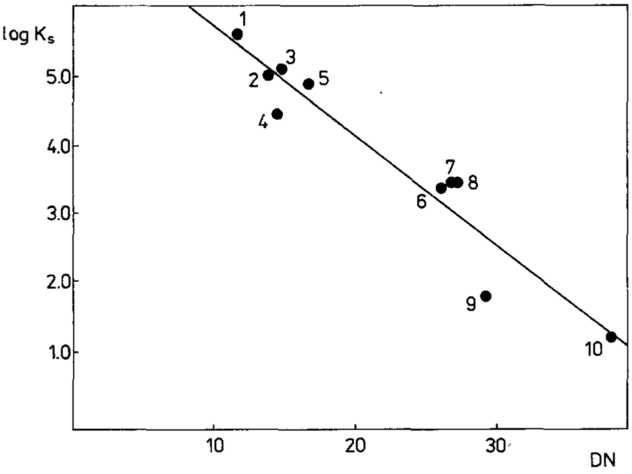

Fig. 1. Dependence of log K_s values of the thallium(I)-18-crown-6 complex on Gutmann donor numbers of solvents (comp. Table 1)

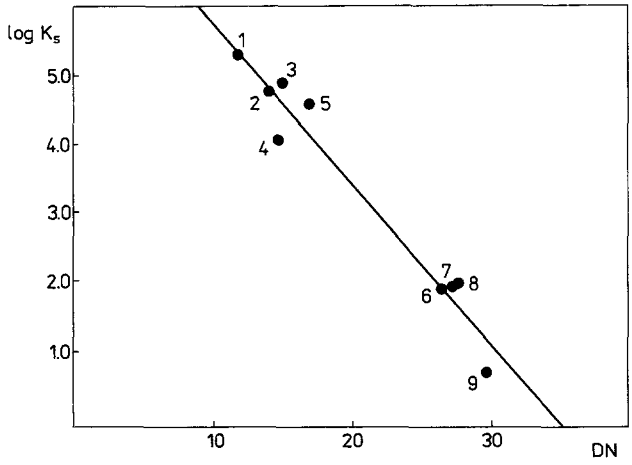

Fig. 2. Plot of log K_s values of thallium(I)-dibenzo-18-crown-6 complex vs. Gutmann donor numbers of solvents (comp. Table 1)

with a correlation coefficient of $R = 0.9806$, and

$$\log K_s = -(0.238 \pm 0.014)\,DN - (0.100 \pm 0.036)\,AN + (9.893 \pm 0.706), \qquad (9)$$

with $R = 0.9905$, for the systems Tl^+-18C6 and Tl^+-DB18C6, respectively. As can be seen, the differences between the correlation coefficients of Eqs. (6) and (8) as well as (7) and (9) are not very significant. So, in order to decide whether the improvement due to addition of the *AN*-parameter is significant, we have employed the F_{imp}-test as proposed in [35]. It follows from these considerations that the improvement of correlation (8) relative to (6) and, similarly, correlation (9) relative to (7) is not statistically significant. Therefore we are allowed to assume that the solvent effect on complex formation in the systems investigated is restricted to the solvation phenomena of cationic species, particularly to the solvation of the thallium(I) ion.

It is noteworthy that numerous adducts of crown ethers with organic molecules have been isolated and identified in solid phase [36]. There are also some informations about the interactions between crown ethers and acetonitrile in solutions [37–40], but no precise data are known up to now. Based on the results presented in this report, it may be assumed that the influence of the ligand-solvent interactions upon the complexation of Tl(I) is negligible. In other words, Eqs. (6) and (7) are acceptable and the deviations from correlation lines may be explained by experimental errors.

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References

[1] De Jong F., Reinhoudt D. N. (1980) Adv. Phys. Org. Chem. **17**: 279

[2] Hiraoka M. (1982) Crown Compounds, Their Characteristics and Applications. Kodanska, Tokyo

[3] Izatt R. M., Bradshaw J. S., Nielsen S. A., Lamb J. D., Christensen J. J., Sen D. (1985) Chem. Rev. **85**: 271

[4] Lee Y. C., Allison J., Popov A. I. (1985) Polyhedron **4**: 445

[5] Lada E., Kalinowski M. K. (1989) Polyhedron **8**: 2115

[6] Mann C. K. (1969) In: Bard A. J. (ed.) Electroanalytical Chemistry, Vol. 3. M. Dekker, New York, ch. 2

[7] Gokel G. W., Cram D. J. (1974) J. Org. Chem. **39**: 6

[8] Mambetkozyiev E. A., Zhdanov S. I. (1980) Uspekhi Khim. **49**: 588

[9] Gupta P. N., Bhat S. A. (1982) J. Electrochem. Soc. India **31**: 171

[10] Crow D. R. (1969) In: Polarography of Metal Complexes. Academic Press, London

[11] Galus Z. (1976) In: Fundamentals of Electrochemical Analysis. Ellis Horwood, Chichester, ch. 14

[12] Prue J. E., Sherrington P. J. (1961) Trans. Faraday Soc. **57**: 1795

[13] Yaeger H. L., Kratochvil B. (1970) J. Phys. Chem. **74**: 963

[14] De Ford D. D., Hume D. N. (1951) J. Amer. Chem. Soc. **73**: 5321

[15] Hofmanova A., Koryta J., Brezina M., Mittal M. L. (1978) Inorg. Chim. Acta **28**: 73

[16] Kolthoff I. M., Chantooni M. K. (1980) Anal. Chem. **52**: 1039

[17] Massaux J., Desreux J. F. (1982) J. Amer. Chem. Soc. **104**: 2967

[18] Lada E., Filipek S., Kalinowski M. K. (1988) Austr. J. Chem. **41**: 437

[19] Koppel I. A., Palm V. A. (1972) In: Chapman N. B., Shorter J. (eds.) Advances in Linear Free Energy Relationships. Plenum Press, London, ch. 5

[20] Krygowski T. M., Milczarek E., Wrona P. K. (1980) J. Chem. Soc. Perkin Trans. II: 1563

[21] Krygowski T. M., Fawcett W. R. (1975) J. Amer. Chem. Soc. **97**: 2143

[22] Reichardt C. (1988) Solvents and Solvent Effects in Organic Chemistry. Verlag Chemie, Weinheim

[23] Drago R. S. (1980) Coord. Chem. Rev. **33**: 251

[24] Drago R. S. (1980) Pure Appl. Chem. **52**: 2261

[25] Maria P. C., Gal J. F. (1985) J. Phys. Chem. **89**: 1296

[26] Lim Y. Y., Drago R. S. (1972) Inorg. Chem. **11**: 202

[27] Olofsson G., Olofsson I. (1973) J. Amer. Chem. Soc. **95**: 7231

[28] Taft R. W., Pienta N. J., Kamlet J., Arnett M. (1981) J. Org. Chem. **46**: 661

[29] Gutmann V., Wychera E. (1966) Inorg. Nucl. Chem. Lett. **2**: 257

[30] Gutmann V. (1978) The Donor-Acceptor Approach to Molecular Interactions. Plenum Press, New York

[31] Hinton J. F., Briggs R. W. (1975) J. Magn. Res. **19**: 393

[32] Mayer U., Gutmann V., Gerger W. (1975) Monatsh. Chem. **106**: 1235

[33] Smetana A. J., Popov A. I. (1980) J. Soln. Chem. **9**: 182

[34] Rounaghi G., Popov A. I. (1981) J. Inorg. Nucl. Chem. **43**: 911

[35] Krygowski T. M., Radomski J. P., Rzeszowiak A., Wrona P. K., Reichardt C. (1981) Tetrahedron **37**: 119

[36] Vogtle F., Sieger H., Muller M. W. (1981) Top. Curr. Chem. **98**: 107

[37] De Boer J. A. A., Reinhoudt D. N., Harkema S., Van Hummel G. J., de Jong F. J. (1982) J. Amer. Chem. Soc. **104**: 4073

[38] Mosier-Boss P. A., Popov A. I. (1985) J. Amer. Chem. Soc. **107**: 6188

[39] Boss R. D., Popov A. I. (1986) Inorg. Chem. **25**: 1747

[40] Buschmann H. J. (1988) J. Soln. Chem. **17**: 277

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