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Electrochemical Study of 18-Crown-6-Tl^+ Complexes in Binary Solvent Mixtures[1]

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Summary. The formation constants, K_S, of the 18-crown-6 complex with thallium(I) ion were studied by polarographic measurements in binary mixtures of acetonitrile, acetone, tetrahydrofuran, and dimethylsulfoxide with water, as a function of the solvent mole fraction. In all the cases, the variation of the stability constant can be described by the empirical relation $\log K_S = a\,[(\varepsilon-1)/(2\varepsilon+1)] + b$ where ε stands for relative permittivity of a given mixture and *a* and *b* mark the regression coefficients. The values of *a* calculated for four series of binary mixtures showed correlation with the Gutmann donor numbers of the neat organic solvents which form the mixture.

Keywords. Crown ether complexes; Binary solvent mixtures.

Elektrochemische Untersuchung von 18-Krone-6-Tl^+-Komplexen in binären Lösungsmittelgemischen

Zusammenfassung. Es wurden die Komplexbildungskonstanten K_S von 18-Krone-6 mit Thallium(I)-Ionen mittels polarographischer Messungen in binären Mischungen von Acetonitril, Aceton, Tetrahydrofuran und Dimethylsulfoxid mit Wasser als Fuktion des Molenbruch an Solvens untersucht. In allen Fällen konnten die Änderung in den Stabilitätskonstanten mittels der empirischen Beziehung $\log K_S = a\,[(\varepsilon-1)/(2\varepsilon+1)] + b$ beschrieben werden, wobei ε für relative Permeabilität einer gegebenen Mischung steht und *a* und *b* die Regressionskoeffizienten darstellen. Der Wert *a* für vier Serien von binären Mischungen zeigte eine Korrelation mit den Gutmann Donorzahlen der reinen organischen Lösungsmittel aus denen die Mischung zusammengesetzt war.

Introduction

Physicochemical properties of solvent mixtures 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 solvent mixtures do not behave as expected from statistical considerations; the observed deviations from ideal behaviour are indicative of the extent of preferential solvation and the existence of specific solvent-solute interactions and solvent structures

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[1] Dedicated to Professor Dr. Victor Gutmann on the occasion of his 70th birthday

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[1 – 5]. Therefore, in order to understand the thermodynamic, kinetic and mechanistic aspects of chemical processes it is necessary to evaluate the relative solvating ability of the two (or more) solvents towards the reacting species.

We wish to report here the stabiliy constants of the thallium(I) complex with 18-crown-6 in binary solvent mixtures of dimethylsulfoxide (*DMSO*) tetrahydrofuran (*THF*), acetone (*AC*) and acetonitrile (*ACN*) with water, as a function of the solvent mole fraction. The Tl(I) ion has been selected as the probe cation, similarly as in our previous works [6 – 8]. The solvents were selected to give a wide range of Lewis basicity and sufficiently high relative electric permittivity ε to avoid ion pair formation phenomena.

In the past years thallium(I) complexes with crown ethers have been studied in a wide variety of pure solvents (for earlier papers see review [9] and corresponding references therein, and additionally [6 – 8, 10, 11]). Consequently, it has become clear that in aprotic conditions the Gutmann donicity scale [12, 13] is particularly useful to describe the solvent effect on the complexation equilibria [8, 10]. 0n the other hand, however, the stabiliy constant of the thallium(I)-benzo-15-crown-5 complex in alcohols was found to depend on $(\varepsilon - 1)/(2\,\varepsilon + 1)$, the Kirkwood function of a solvent [7].

So far the data for stability of Tl(I)-crown complexes in mixed solvents are not available in the literature; an interesting paper [14] exists on the cryptate $\mathrm{Tl(2,2,2)^+}$ in water-acetonitrile systems. In the last case the stability constant was found to increase with increasing *ACN* content. Much more attention has been paid to the complexation of alkali metal ions by macrocyclic ligands, particulary by crown ethers and cryptands, in binary solvent mixtures [15 – 22]. Although the changes in the formation constant with solvent composition were observed in all studied cases, the influence of physicochemical parameters of mixed solvents on the complexation equilibria was not analysed so far. Such analysis is presented in this communication. As in our previous investigations [6 – 8] the formation constants were calculated from polarographic measurements.

Experimental Part

Polarographic and cyclic voltammetric curves were determined in a three-electrode system with the use of a Radelkis OH 105 apparatus. The potentials were measured against an aqueous s.c.e. Tetrabuthylammonium perchlorate (0.05 mol dm^{-3}) was used as background electrolyte.

All solvents were dried as described elsewhere [23] and fractionally distilled at reduced pressure under an argon atmosphere immediately prior to use. The measurements were performed at a temperature of 23 ± 0.1°C. All remaining experimental details have previously been described [6, 7].

Results and Discussion

When metal ions in solutions are complexed with ligands other than solvent molecules, their polrographic reduction waves are altered in two ways: i) the half-wave potential is shifted in the more negative direction, and ii) the diffusion current changes usually become smaller. For the one-electron reversible reduction occuring at amalgam, the shift in half-wave potential produced by the presence of an excess of ligand L is given by [24]

$$E^{\circ}_{1/2} - E_{1/2} = (RT/F)\ln(K_S c_L) + (RT/F)\ln(i_{LM}{}^{+}/i_M{}^{+}) \qquad (1)$$

Table 1. $\log K_s$ values of 18-C6-Tl$^+$ complexes in binary solvent mixtures; x_s mole fraction of organic solvent

x_s	$\log K_s$			
	ACN-H_2O	*AC*-H_2O	*THF*-H_2O	*DMSO*-H_2O
1.0	5.00 ± 0.08	4.88 ± 0.03	–	1.88 ± 0.02
0.9	4.95 ± 0.04	5.56 ± 0.02	–	2.34 ± 0.02
0.8	5.01 ± 0.01	5.57 ± 0.02	–	2.48 ± 0.01
0.7	4.58 ± 0.03	5.27 ± 0.02	–	2.63 ± 0.03
0.6	4.17 ± 0.04	5.08 ± 0.02	3.75 ± 0.05	2.76 ± 0.03
0.5	3.66 ± 0.03	4.57 ± 0.02	3.73 ± 0.01	3.08 ± 0.02
0.4	3.58 ± 0.02	3.85 ± 0.03	3.63 ± 0.02	3.21 ± 0.01
0.3	3.26 ± 0.01	3.40 ± 0.01	3.28 ± 0.02	3.30 ± 0.01
0.2	3.11 ± 0.05	3.22 ± 0.04	2.86 ± 0.02	3.41 ± 0.01
0.1	2.85 ± 0.01	2.74 ± 0.01	2.64 ± 0.02	–

when K_S is the stability constant, $E^\circ_{1/2}$ stands for the potential of the process

$$M_{solv} + e^- \rightleftharpoons M_{(Hg)} \tag{2}$$

$E_{1/2}$ is the potential determined at a given c_L, the concentration of L, whereas the ratio $i_{LM}{}^+/i_M{}^+$ is attributed to a change in the diffusion coefficient of M^+ upon complexation. The assumption made in deriving equation (1) is that the complexation is of 1 : 1 type; for this case a value of $\Delta\Delta E_{1/2}/\Delta \log c_L = -59\,\mathrm{mV}/\log c_L$ may be predicted.

Thallium(I) is reduced at a dropping mercury electrode forming a single diffusion controlled wave in all the media under study (see e.g. Ref. [25]). The shapes of the cyclic voltammetric curves are in agreement with those characteristic for reversible one electron transfer both in the absence and presence of 18-crown-6, the complexing agent. Addition of the ligand shifts the $E^\circ_{1/2}$ values in a negative direction indicating that only the 1 : 1 complex is formed in solutions; the value of $\Delta\Delta E_{1/2}/\Delta \log c_L$ was found to be $-57 \pm 5\,\mathrm{mV}$ in all the solvents under study.

Table 1 summarizes the stabililty constants calculated according to Eq. (1), whereas the variations of the $\log K_S$ values as a function of solvent composition are shown in Fig. 1. It should be emphasized that the already published result for the complex in pure *DMSO* agrees well with the value presented in this table [10].

First attention is paid to the values of the stability constants in *DMSO*-water mixtures. As can be seen from Fig. 1 the $\log K_S$ values increase monotonically as the mole fraction of the organic solvent (x_{DMSO}) is lowered. The observed trend is not particularly surprising: the degree of complexation should indeed be greater in water as less basic solvent than in *DMSO* in which thallium(I) cations are more strongly solvated. However, this is in agreement with a study of the ^{205}Tl(I) resonance frequency in pure solvents (among of these in H_2O and *DMSO*) and in the *DMSO*-H_2O binary mixtures [26, 27]. Also this is confirmed by the stability constants of the 18 C6-Tl$^+$-complex in neat *DMSO* and water: corresponding $\log K_S$ values are 1.88 (Table 1) and 2.27 [15], respectively. It is then clear that the behaviour of the complex agrees well with the solvating ability of various *DMSO*-H_2O systems.

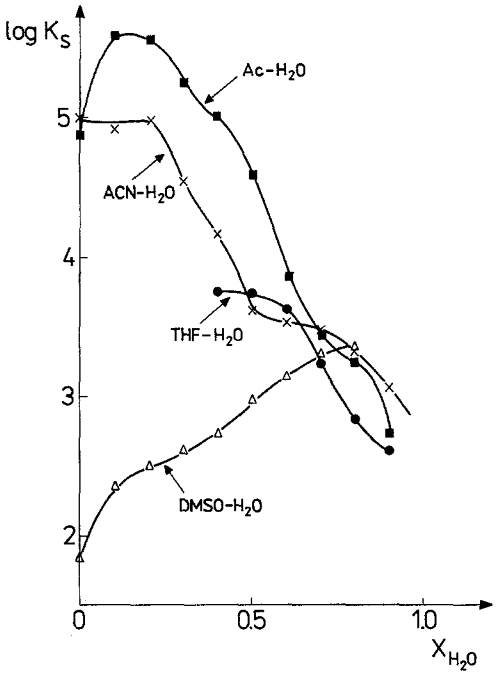

Fig. 1. Variation of the stability constants of the 18-C6-Tl$^+$ complex with solvent composition in binary mixtures; x_{H_2O} is the molar fraction of water

Generally, two basic viewpoints on the principles of solvation phenomena are known. According to the first, the solvent is considered as an isotropic continuum which surrounds the molecules and/or ions of the solute. A solvent effect of this type is connected with long-range forces and is often considered in terms of universal or non-specific solvent-solute interactions. The intensity of such interactions is determined by macroscopic physical parameters of the solvent i.e. relative permittivity and refractive index. Next, accordingly to the second model, the solvent should be assumed as anisotropic and inhomogeneous, and these features determine the nature of so called specific solvation effects. Such solvent-solute interactions are chemical (short-range) in nature and consist of the formation of solvation complexes through donor-acceptor bonds which are localised and directed in space in a definite manner.

Both two basic concepts are complementary. This is reflected by the well known four-parameter equation of Koppel and Palm [28] which was successfully used by many authors to interpret the solvent effects on various physicochemical properties of dissolved compounds (see e.g. monograph [29]). Note that this equation is similar to that of Abraham, Kamlet and Taft and their coworkers [30, 31] who proposed a corresponding relation based on a more sophisticated theory of solutions.

Historically, various model processes have been tested to interpret the specific solvation effects. However, since the pioneer studies of Gutmann in 1966 on the scale of solvent donicity, a very large number of investigations based on the donor-acceptor concept have been published. Consequently, the rate and equilibrium data for many processes occuring in a number of solvents were found to reflect the effective solvating ability expressed in categories of specific solvation.

The term "donicity" was proposed by Gutmann to describe the ability of solvents to donate electron pairs to acceptor solutes. The donor number, *DN*, was introduced as a measure of the donicity [12]; it is the negative enthalpy of the formation of the 1 : 1 adduct $SbCl_5$-solvent in 1,2-dichloroethane. Nowadays, despite criticism of either the concept [32, 34] or some experimental values [34–37] the donor number is one of the most widely used empirical parameters of solvent basicity (cf. monographs [2, 29, 38]), particularly in the field of coordination chemistry [1, 13, 39, 40].

Table 2. Relative permittivities ε^a and empirical Lewis basicity parameters β^b for mixtures of organic solvents with water^c

x_s	*ACN*-H_2O		*AC*-H_2O		*THF*-H_2O		*DMSO*-H_2O	
	ε	β	ε	β	ε	β	ε	β
1.0	35.9	0.37	20.7	0.54	7.6	0.54	46.7	0.76
0.9	37.6	0.40	21.7	0.54	8.1	0.49	49.9	0.79
0.8	39.3	0.43	22.6	0.54	8.6	0.45	53.6	0.77
0.7	41.4	0.44	25.3	0.55	10.2	0.43	56.4	0.70
0.6	44.0	0.42	28.5	0.56	13.3	0.43	59.1	0.66
0.5	47.1	0.40	32.4	0.57	18.1	0.41	62.3	0.62
0.4	50.8	0.40	37.2	0.54	24.4	0.43	65.9	0.56
0.3	55.7	0.41	43.3	0.51	32.3	0.47	70.0	0.50
0.2	62.3	0.39	51.5	0.47	41.8	0.52	73.8	0.45
0.1	70.5	0.34	62.6	0.42	52.8	0.55	76.9	0.35

[a] See Table 7.1 in Ref. [44] and references therein

[b] Taken from Ref. [48]

[c] For abbreviations cf. Table 1

Strictly speaking, the *DN* scale seems to be fully justified for aprotic solvents; it has been established many times that dissimilar acceptors do yield linear relationships between the measured quantities and *DN* values. It should be noted only that the donicity scale does not take into account the "hard-soft" interactions between donors and acceptors (for a discussion of this problem see for example [41]). However, for many solvents the *DN* can be replaced by others indices of the solvent basicity [42–44]. Among these, a quantity that has been strongly promoted is the β-scale obtained by the solvatochromic method of Kamlet, Taft and coworkers [45, 46]. The conclusion from the considerations of Marcus [44] is that the β and *DN* scales seem to measure the donicities of solvents equally succesfully as far as the solvents are not strongly structured.

On the other hand, the validity of *DN* for protolytic solvents, as e.g. water and alcohols, is less clear. For example, the Gutmann donor number for water is 18 [13], whereas the secondary *DN* value obtained from the ^{23}Na(I) resonance data – uncorrected for magnetic susceptibiliy – was found to be close to 33. The value corrected is still higher and equal to 38 [47]. In our opinion however, all these values are correct since in both cases the acceptor molecules show different strength, and, generally, one should expect that in the case of highly structured solvents their basicity parameters must be dependent on the type of the probe molecule.

The *DN* values for mixed solvents were not measured, whereas the β values of some aqueous binary solvent mixtures are available in the literature [48]. For the systems investigated by us, the data are collected in Table 2 together with the relative permittivities being also of interest in the context of the present communication.

Let us return to our experimental results. The values of the $\log K_S$ listed in Table 1 for the *DMSO*-H_2O mixtures were regressed against the $(\varepsilon-1)/(2\varepsilon+1)$ parameter and we have obtained regression in the following form

$$\log K_S = 256.82\,(\pm 13.90)\,[(\varepsilon-1)/(2\varepsilon+1)] - 123.33\,(\pm 6.77) \qquad (3)$$

with a correlation coefficient of $r=0.9901$ and a standard deviation of $s=0.06$ (errors in paranthesis are standard deviations).

An excellent linear correlation between the $\log K_S$ and $(\varepsilon-1)/(2\varepsilon+1)$ values expressed by Eq. (3) (Fig. 2) seems to indicate the decisive role of non-specific solvation interactions. However, such a suggestion is not true; in correlating the solvent changes of $\log K_S$ in the *DMSO*-H_2O mixtures the solvent basicity is also important. In fact, the $(\varepsilon-1)/(2\varepsilon+1)$ and β values for our binary mixtures are colinear to a high degree; for nine solvent systems from Table 1 the following relationship exists

$$\beta = -67.90(\pm 8.48)[(\varepsilon-1)/(2\varepsilon+1)] + 33.72(\pm 4.14) \qquad (4)$$

with $r = 0.9432$. Thus, it is not surprising that the $\log K_S$ values can also be correlated with β, and we have found the linear regression in the form of Eq. (5):

$$\log K_S = -3.80(\pm 0.62)\beta + 5.24(\pm 0.41) \qquad (5)$$

with $r=0.9169$ and $s=0.19$. Therefore the relative importance of different types of solvation cannot be recognized.

Qualitatively, a similar situation exists also in the *THF*-H_2O and *AC*-H_2O binary mixtures; the role of the $(\varepsilon-1)/(2\varepsilon+1)$ and β terms seems to be comparable. It is noteworthy, therefore, that we have found linear correlations in the form of Eq. (6) and (7) for the *THF*-H_2O and *AC*-H_2O solvent systems, respectively (Fig. 2):

$$\log K_S = -27.19(\pm 7.63)[(\varepsilon-1)/(2\varepsilon+1)] + 16.10(\pm 3.59) \qquad (6)$$

with $r=0.8720$ and $s=0.21$ and

$$\log K_S = -115.85(\pm 15.72)[(\varepsilon-1)/(2\varepsilon+1)] + 59.53(\pm 7.48) \qquad (7)$$

with $r=0.9336$ and $s=0.35$.

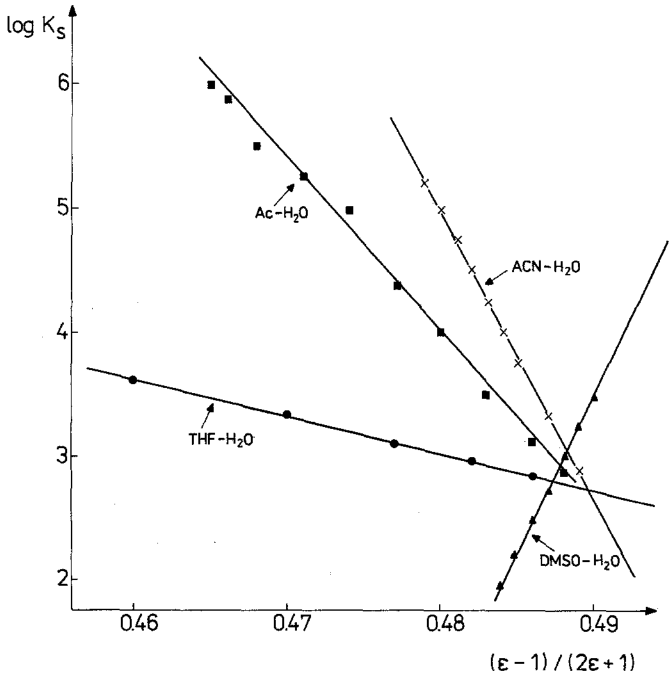

Fig. 2. Dependence of the stability constants of the 18-C6-Tl$^+$ complex on the polarity function for solvent mixtures

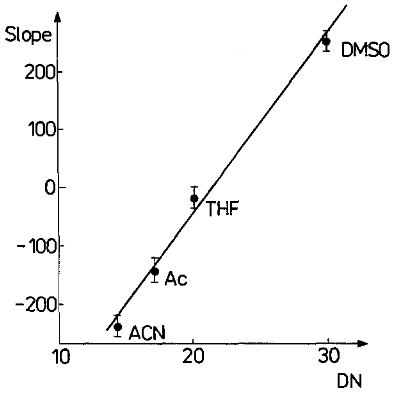

Fig. 3. Plot of the slopes of regressions presented in Fig. 2 vs. the Gutmann donor numbers of neat organic solvents

It is assumed that the components of the mixed solvents interact with the solute both by the mechanisms of non-specific and specific solvation.

Only for the acetonitrile-water solvents, the contribution of the basicity seems to be less important than that of the dielectric term. In these solvent systems the terms $(\varepsilon-1)/(2\varepsilon+1)$ and β are worsely correlated and the correlation coefficient between them is $r=0.435$. Consequently, a satisfactory correlation between $\log K_S$ and $(\varepsilon-1)/(2\varepsilon+1)$ is observed [Eq. (8), Fig. 2]. In fact

$$\log K_S = -241.95(\pm 17.88)[(\varepsilon-1)/(2\varepsilon+1)] + 121.12(\pm 8.66) \qquad (8)$$

with $r=0.9788$ and $s=0.16$, whereas a relationship of $\log K_S$ versus β does not exist ($r=0.4500$).

What is, however, the physical meaning of our correlations? As it was pointed out above, the interdependence between the $(\varepsilon-1)/(2\varepsilon+1)$ and β values do not permit to separate the effects of specific and non-specific solvation. It is also evident, that besides the solvation equilibria involving the molecules and ions of solvent and solute, similar equilibria may involve the interaction of the components of the solvent mixtures alone. A property that is relevant to the solvation is the solvent structure. In the case of water, structural studies and computer simulations provided very important results, but such informations concerning neat nonaqueous solvents are almost totally lacking (cf. Ch. 5 and 6 in Ref. [2] and references therein). Of course, there is doubt that as two solvents are mixed the homo-aggregates are broken up with the formation of hetero-agregates, but our quantitative knowledge on this subject is still very rudimentary. And these are the reasons for which Eqs. (3) and (6) – (8) should be considered as purely empirical treatments. Nevertheless, all these regressions have a "robust" character and predict satisfactorily the influence of the medium composition on the $\log K_S$ values.

Finally it is interesting to observe that the slopes of regressions presented in Fig. 2 are clearly dependent on the nature of neat organic solvents. Of course, such a slope has a physical meaning of the degree of differentiation of the 18C6-Tl$^+$ complex stability due to the changes in the composition of solvent mixtures. This differentiation becomes greater with increase of the basicity of pure solvents, and hence it would seem reasonable to plot the slopes of Eqs. (3) and (6) – (8) versus the Gutmann donor numbers. In fact, Fig. 3 shows that satisfactory correlation exisis.

This behaviour is connected with the inherent solvating ability of the neat solvents which form the mixture.

Acknowledgements

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