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Complexing Equilibria and Redox Potentials in the System Ag(II)/Ag(I)-1,10-Phenanthroline in Propylene Carbonate

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Predominance areas of various equilibria were identified and complex formation constants of Ag(I) with 1,10-phenanthroline were determined as well as the solubility product of the complex salt for Ag(*phen*)$_2$ClO$_4$ in propylene carbonate. The solubility product of AgNO$_3$ in propylene carbonate was estimated. The value of the formal potential of the system Ag(*phen*)$_2^{2+}$/Ag(*phen*)$_2^+$ in *PC* was determined by chronovoltammetry. Differences in the stability of analogous complexes in water and *PC* are discussed.

(Keywords: Chronovoltammetry; Formal potential; Potentiometry; Propylene carbonate; Redox systems with silver ions; Stability of complexes)

Die Gleichgewichtskonstante der Komplexierung und die Redoxpotentiale im System Ag(II)/Ag(I)-*1,10-Phenantrolin in Propylencarbonat*

Die Gebiete der Dominanz der einzelnen Gleichgewichte, die Bildungskonstanten β_1 und β_2 der Komplexe Ag(I) mit 1,10-Phenantrolin und der Wert des Löslichkeitsproduktes Ag(*phen*)$_2$ClO$_4$ in Propylencarbonat wurden bestimmt. Das Löslichkeitsprodukt von AgNO$_3$ in Propylencarbonat wurde abgeschätzt. Die Werte des formalen Potentials des Systems Ag(*phen*)$_2^{2+}$/Ag(*phen*)$_2^+$ in *PC* wurden mit Hilfe cyclischer Voltametrie ermittelt. Es wurden weiterhin die Unterschiede in der Stabilität analoger Komplexe in Wasser und in Propylencarbonat diskutiert.

Introduction

A considerable amount of basic research has been devoted in recent years to the complexing of silver ions and redox systems of the type: AgL_2^{2+}/AgL_2^+ in nonaqueous solutions such as acetonitrile and propylene carbonate [1–9]. The development is related to the attempts to use these systems in organic synthesis, where nonaqueous solvents generally suppress the destruction and the formation of oxygen derivatives in oxidation products.

On the basia of our earlier results on the characteristics of the Ag(II)/Ag(I) systems arising with 2,2'-bipyridine, 1,10-phenanthroline and pyridine in water and in acetonitrile [8, 10–12] we were able to specify the conditions for the redox systems with a constant standard potential in different solvents [9]. It follows from our studies that the $Ag(phen)_2^{2+}/Ag(phen)_2^+$ system should have a different standard potential in water, acetonitrile and propylene carbonate. Hence, the object of the present investigation was a description of the equilibria occuring in the system Ag(II)/Ag(I) in the presence of 1,10-phenanthroline and a characteristic of the redox system $Ag(phen)_2^{2+}/Ag(phen)_2^+$ in propylene carbonate.

Experimental

$Ag(phen)_2NO_3$-di-(1,10-phenanthroline)silver(I) nitrate was obtained from 0.1 *M* solution of $AgNO_3$ by precipitation with an excess of phenanthroline.

$Ag(phen)_2(NO_3)_2$-di-(1,10-phenanthroline)silver(II) nitrate was obtained using a procedure identical to the *Thorpe* and *Kochi* method [13]. The compound was purified and its purity tested by the method described previously [12].

Anhydrous $AgClO_4$ was obtained from analytically pure Ag_2CO_3 crystallized from water followed by triple crystallization from acetonitrile. The required amount of propylene carbonate was added to a saturated solution of $AgClO_4$ in acetonitrile and acetonitrile was evaporated at 80 °C under reduced pressure.

$(C_2H_5)_4NNO_3$ and $(C_2H_5)_4NClO_4$ were obtained as described by *Kolthoff* [14]. The products were crystallized triply from water followed by single crystallization from acetonitrile and dried under vacuum at room temperature.

Propylene carbonate (Merck) was purified in a way similar to *Salamon*'s procedure [15]. The solvent was dried for three days above molecular sieves Linde 4 Å and by means of CaH_2 for another three days. Following that there were two runs of fractional distillation under 3–4 mm Hg, with the intermediate 2/3 of the distillate fraction being collected and directly transformed to argon atmosphere. The purity of the final product, checked by spectrometry and chromatography, was found to comply with the criteria of *Fujinaga* and *Izutsu* [16].

The other reagents were analytically pure (P. O. Ch. Gliwice). The apparatus employed in the potentiometric and chronovoltammetric investigation has been described in earlier papers [10, 12].

Methods and Results

Potentiometric Investigation and Nernst's Equation for Ag^+ *Ions in Propylene Carbonate*

Potentiometric investigations in nonaqueous solutions require the use of a stable reference electrode reversible in the given solution. Of those employed in propylene carbonate the most suitable seems to be the $Ag/AgClO_4$ electrode. In addition to retaining its stability for a number of weeks, being easy to make and store [17, 18], it gives rapid potential response and ensures good reproducibility of the results. The most frequently used supporting electrolyte is $(C_2H_5)_4NClO_4$ (similar ion mobility) or $LiClO_4$, easily soluble in *PC*. In our investigations, in view of the precipitation of sparingly soluble Ag(*phen*)$_2$ClO$_4$, we found it necessary to use tetraethylammonium nitrate.

The dependence of the potential on the concentration of Ag^+ ions in *PC* was investigated by *Butler* [19] and *Gileadi* [18]. In the system:

Ag/Ag^+ + 0.1 *M* $(C_2H_5)_4NClO_4$—reference electrode and 0.1 *M* $(C_2H_5)_4NClO_4$—supporting electrolyte *Butler* found the *Nernest* equation to be applicable in the concentration range from 10^{-3} to $8.5 \cdot 10^{-2}$ *M* Ag^+ at the slope of 58 mV. *Gileadi's* studies demonstrate that the relation is fulfilled in the range from $2 \cdot 10^{-3}$ to 10^{-1} *M* Ag^+ with the slope of 67 mV in 0.2 *M* $LiClO_4$ and 65 mV in 0.1 *M* $LiClO_4$. In the case of lower Ag^+ ion concentrations the time of potential stabilisation is quite considerable and the reproducibility of the results amounts to 5 mV.

Nevertheless, at a supporting electrolyte concentration of less than 0.1 *M* the *Nernst* equation is satisfied up to the concentration of $5 \cdot 10^{-5}$ *M* with the slope of 60 mV.

We carried out analogous studies using $(C_2H_5)_4NNO_3$ as supporting electrolyte and the cell:

$$Ag/0.01\,M\,AgClO_4(PC) + 0.1\,M(C_2H_5)_4NNO_3(PC) \parallel$$
$$0.1\,M(C_2H_5)_4NNO_3(PC) \parallel c\,Ag^+(PC) + 0.1\,M(C_2H_5)_4NNO_3(PC)/Ag$$

where *c* denotes the concentration of Ag^+ ions in the range from $5 \cdot 10^{-6}$ to $5 \cdot 10^{-2}$ *M* established by means of 0.7625 *M* solution of $AgClO_4$ in *PC* at $T = 298$ K.

The results of measurements for concentrations of Ag^+ ions from $3 \cdot 10^{-2}$ *M* to $5 \cdot 10^{-3}$ *M* are not very reliable involving a considerable error (slope of 85 ± 3 mV), while for concentrations above $3 \cdot 10^{-2}$ *M* the *Nernst* equation is not satisfied. The *EMF* values are stable and well reproducible in the range from $5 \cdot 10^{-6}$ *M* to $3.8 \cdot 10^{-3}$ *M* Ag^+; at $T = 298$ K the slope is 59.9 ± 0.4 mV.

Complexing and Precipitation Equilibria in the Ag(I)-*1,10-Phenanthroline System*

The measurements were carried out in the system:

$$Ag/0.01\,M\,AgClO_4(PC) + 0.1\,M(C_2H_5)_4NNo_3(PC) \parallel$$
$$0.1\,M(C_2H_5)_4NNO_3(PC) \parallel c_L phen(PC) + c\,AgClO_4(PC)$$
$$+ 0.1\,M(C_2H_5)_4NNO_3(PC)/Ag$$

with variable concentrations of $AgClO_4$ and phenanthroline from $c^0_H/c^0_{Ag^+} = 100$ to $c^0_H/c^0_{Ag^+} = 1$, so that the experimentally determined Ag^+

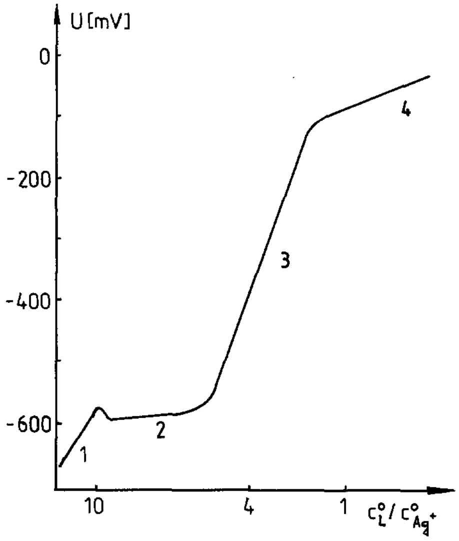

Fig. 1. An example of a potentiometric titration curve for a 10^{-2} M solution of 1,10-phenanthroline titrated with silver perchlorate in propylene carbonate; the digits denote the succesive equilibrium ranges

ions concentrations (following the establishment of all equilibria) were in the range from $5 \cdot 10^{-6}$ M to $3.8 \cdot 10^{-3}$ M.

The potentiometric curves of the titration of phenanthroline with silver perchlorate looked like those presented as an example in Fig. 1.

Four distinct equilibrium regions can be distinguished on these curves, which depend on the $c^0_L/c^0_{Ag^+}$ concentration ratios.

In region 1 ($c^0_L/c^0_{Ag^+} \gg 1$) we are dealing with the formation of a soluble Ag(*phen*)$_2^+$ complex. With the increase of K_{so} there arises a white precipitate of the complex salt Ag(*phen*)$_2$ClO$_4$ (region 2). In region 3 ($c^0_L/c^0_{Ag^+} \approx 4$) diphenanthrolinesilver(I) perchlorate dissolves and complex Ag(*phen*)$^+$ arises. Finally, region 4 illustrates the formation of the complex Ag(*phen*)$^+$ in the absence of any other conditioning factors.

Determination of the conditional complex formation constant β_2

Under conditions of considerable excess of ligand concentration in region 1 of the titration curves there arises a soluble complex of the type AgL_2^+ in accordance with the equation:

$$Ag^+ + 2\,phen \overset{\beta_2}{\rightleftharpoons} Ag(phen)_2^+$$

(The results of measurements rule out the formation of complexes with higher coordination number.) The value of the conditional constant of $\beta_{2(0.1)}$ of complex formation and the composition of the complex were determined in the generally accepted way. The results are presented in Table 1.

Table 1. *Results of measurements of the conditional complex formation for* $Ag(phen)_2^+$ *in propylene carbonate* [$\mu = 0.1 - (C_2H_5)_4NNO_3$, $T = 298$ K]

$c^0_{Ag^+} \cdot 10^{-4}$ (mol/dm^3)	$c^0_L/c^0_{Ag^+}$	U (V)	$c_{exp} \cdot 10^{-13}$ (mol/dm^3)	$\beta_2 \cdot 10^{12}$
0.9901	100	−0.6456	0.3914	2.45
1.9608	50	−0.6269	0.8032	2.69
2.9126	33.33	−0.6137	1.3342	2.69
3.8462	25	−0.6046	1.8929	2.57
4.7619	20	−0.5961	2.6244	2.47
5.6604	16.67	−0.5899	3.3307	2.46
6.9767	13.33	−0.5823	4.5608	2.50
7.4074	12.5	−0.5799	4.8920	2.49
8.2569	11.11	−0.5749	5.9286	2.46

The c_{exp} values in Table 1 denote the Ag^+ ion concentrations following the establishment of complexing equilibrium, determined from *Nernst*'s equation.

$$\bar{\beta}_{2(0.1)} = (2.53 \pm 0.2) \cdot 10^{12}$$

Determination of the Solubility Product for $Ag(phen)_2ClO_4$

As more Ag^+ ions are added to the solution under investigation, the concentration of ClO_4^- ions increases, on the titration curve one can see a potential jump and a plateau arising as a result of complex salt precipitation.

The equilibria characteristic of this region may be represented by the equations:

$$Ag^+ + 2\,phen \overset{\beta_2}{\rightleftharpoons} Ag(phen)_2^+ \qquad \text{(I)}$$

$$Ag(phen)_2^+ + ClO_4^- \overset{K_{so}}{\rightleftharpoons} Ag(phen)_2ClO_4 \qquad \text{(II)}$$

$$K_{so}^{-1} = \beta_2 c_{exp}^2 [L]^2 \{1 + \beta_2 [L]^2\} \qquad (1)$$

where K_{so} is the constant of precipitate formation and $[L]$ is the ligand equilibrium concentration.

Under the conditions of the measurements, $\beta_2 \cong 10^{12}$, and the phenanthroline concentration $[L] \cong 10^{-3}$ *M*, hence Eq. (1) can be reduced to

$$K_{so}^{-1} = \beta_2^2 c_{exp}^2 [L]^4 \qquad (2)$$

For a complex with coordination number -2

$$[L] = c_L^0 - 2\, c_{compl}$$

moreover, for $c_L^0/c_{Ag^+}^0 \approx 4$ (region 2) and for negligible small c_{exp} values ($\sim 10^{-12}$ *M*) it can be assumed that $c_{compl} = c^0_{Ag^+}$, hence the final form of the equation is

$$K_{so}^{-1} = \beta_2^2 c_{exp}^2 (c_L^0 - 2\, c^0_{Ag^+})^4 \qquad (3)$$

No account was taken here of the association of Ag(I) salts in propylene carbonate; $AgClO_4$ is, as has been demonstrated by *Courtot-Coupez* [20], a strong electrolyte in this solvent, while the values r_c of ion pairs formation (3.52 Å for H_2O and 4.2 Å for *PC*) [21] and the above discussion of the *Nernst* equation points to the same character of $AgNO_3$.

The results of the measurements are collected in Table 2.

Table 2. *Results of measurements of the conditional constant of* Ag(*phen*)$_2$ClO$_4$ *precipitate formation in propylene carbonate* [$\mu = 0.1 - (C_2H_5)_4NNO_3$, $T = 298$ K]

$c^0_{Ag^+} \cdot 10^{-3}$ (mol/dm^3)	$c^0_L/c^0_{Ag^+}$	U (V)	$c_{exp} \cdot 10^{-12}$ (mol/dm^3)	$K_{so}^{-1} \cdot 10^{-8}$
0.9910	9.09	−0.6009	2.1822	7.39
1.0714	8.33	−0.6004	2.2245	6.67
1.2281	7.41	−0.5967	2.5646	6.69
1.3793	6.67	−0.5925	3.0139	6.87
1.5254	5.88	−0.5865	3.7958	7.98
1.6667	5.26	−0.5822	4.4780	8.02
1.8033	4.76	−0.5791	5.0449	7.54
1.8655	4.35	−0.5762	6.6396	7.56

The solubility product for Ag(*phen*)$_2$ClO$_4$ in *PC* obtained in this study is:

$$K^{-1}_{so(0.1)} = (7.34 \pm 0.2) \cdot 10^{-6}$$

Determination of the Conditional Complex Formation Constant — β_1 and the Equilibrium Constant of Ag(*phen*)$_2$ClO$_4$ Dissolution

The curves of the titration of phenanthroline solutions with silver perchlorate indicate that with increasing Ag^+ ion concentrations (for concentration ratios $c_L^0/c_{\mathrm{Ag}^+}^0 < 4$) there takes place dissolution of $\mathrm{Ag}(phen)_2\mathrm{ClO}_4$ and simultaneous formation of $\mathrm{Ag}(phen)^+$ complex. The equilibria obtained in this range can be described by the equations:

$$\mathrm{Ag}(phen)_2\mathrm{ClO}_4 + \mathrm{Ag}^+ \overset{K}{\rightleftharpoons} 2\,\mathrm{Ag}(phen)^+ + \mathrm{ClO}_4^- \qquad \text{(III)}$$

$$\mathrm{Ag}^+ + phen \overset{\beta_1}{\rightleftharpoons} \mathrm{Ag}(phen)^+ \qquad \text{(IV)}$$

Taking into account the equilibria (I)–(IV), the equilibrium constant K can be written as

$$K = \frac{\beta_1^2}{\beta_2 K_{\mathrm{so}}} \qquad (4)$$

It follows from Eq. (4) that in order to determine the value of K one needs to know the value of β_1.

Since total dissolution of the complex salt precipitate took place at large excess of Ag^+ ions (a concentration extending beyond the applicability of *Nernst*'s equation), the constant of complex formation for $\mathrm{Ag}(phen)^+$ was determined from independent measurements for $c_L^0 = c_{\mathrm{Ag}^+}^0$ in the order of 10^{-4} *M*.

The results of the measurements are collected in Table 3.

$$\bar{\beta}_{1(0.1)} = (5.22 \pm 0.3) \cdot 10^4$$
$$\bar{K}_{(0.1)} = (1.92 \pm 0.1) \cdot 10^{-5}$$

Table 3. *Results of measurements of the conditional complex formation for* $\mathrm{Ag}(phen)^+$ *in propylene carbonate* [$\mu = 0.1 - (\mathrm{C_2H_5})_4\mathrm{NNO_3}$, $T = 298$ K]

$c_L^0 = c_{\mathrm{Ag}^+}^0 \cdot 10^{-4}$ (mol/dm^3)	U (V)	$c_{\mathrm{exp}} \cdot 10^{-5}$ (mol/dm^3)	$c_{\mathrm{compl}} \cdot 10^{-4}$ (mol/dm^3)	$\beta_1 \cdot 10^4$	$K \cdot 10^{-5}$
5.000	−0.1446	9.05	4.095	5.00	2.00
4.000	−0.1482	7.883	3.212	5.16	1.94
3.333	−0.1515	6.945	2.639	5.47	1.83
2.857	−0.1535	6.432	2.214	5.35	1.87
2.500	−0.1550	6.072	1.893	5.13	1.95

Estimation of the Conditional Constant of $\mathrm{AgNO_3}$ *Precipitate Formation*

The value of the solubility product for $\mathrm{Ag}(phen)_2\mathrm{ClO}_4$ made it impossible to use $(\mathrm{C_2H_5})_4\mathrm{NClO_4}$ as the supporting electrolyte. At ClO_4^- concentration of 0.1 *M* the titration curves revealed a $\mathrm{Ag}(phen)_2\mathrm{ClO}_4$ precipitate even at negligibly small Ag^+ ion concentrations. Under such conditions the values of β_2 and K_{so} cannot be determined. It was thus necessary to employ $(C_2H_5)_4NNO_3$ as the supporting electrolyte. In the course of our attempts to obtain solutions of silver salts in propylene carbonate we noted low solubility of $AgNO_3$.

As could have been expected, in a series of measurements for ionic strength $\mu = 0.1$ $(C_2H_5)_4NNO_3$ the titration curves showed—following region 4—a potential drop corresponding to $AgNO_3$ precipitation. The value of $K^{-1}_{so(0.1)}$ initially estimated for $AgNO_3$ in *PC* to be equal to $7 \cdot 10^{-3}$ requires—under the conditions of measurements—the presence of Ag^+ ions with a concentration of $\sim 7 \cdot 10^{-2}$ *M* so that the solubility product can be obtained. It follows from the results presented above that in this range of concentrations a direct potentiometric estimation of K_{so} is practically impossible.

All one can do is to estimate that value based on the potential drops of the titration curves and on visual observation. The values of Ag^+ ions concentration corresponding to the potential drops and the estimated values of K_{so} are collected in Table 4.

The solubility product for $AgNO_3$ in propylene carbonate is:

$$K^{-1}_{so(0.1)} = (6.9 \pm 2) \cdot 10^{-3}$$

Table 4. *Estimated conditional constant of precipitate formation for* $AgNO_3$ *in propylene carbonate* [$\mu = 0.1 - (C_2H_5)_4NNO_3$, $T = 298$ K]

$c_{Ag^+} \cdot 10^{-2}$ (mol/dm^3)	c_{NO-_3} (mol/dm^3)	$K^{-1}_{so AgNo3} \cdot 10^{-3}$ (mol/dm^3)
5.25	0.1	5.25
6.06	0.1	6.06
6.87	0.1	6.87
7.66	0.1	7.66
8.81	0.1	8.81

Chronovoltammetric Investigations

Voltamperograms of $5 \cdot 10^{-4}$ *M* solutions of the Ag(*phen*)$_2$NO$_3$ complex and $5 \cdot 10^{-4}$ *M* solutions of the Ag(*phen*)$_2$(NO$_3$)$_2$ complex were carried out in the range of potentials of 10–1 000 mV vs. Ag/0.01 *M* $AgClO_4$. The ionic strength of both solutions was $\mu = 0.1/(C_2H_5)_4NNO_3$.

The curves were recorded relative to the electrode

$$Ag/0.01\,M\,AgClO_4(PC) + 0.1\,M\,(C_2H_5)_4NNO_3(PC)$$

as the reference electrode, with a bridge containing 0.1 *M* $(C_2H_5)_4NNO_3$ in *PC*.

Table 5. *Formal and peak potentials vs.* Ag/*0.01 M* $AgClO_4(PC)$ + *0.1 M* $(C_2H_5)_4NNO_3$ *(PC) for 5 ·10⁻⁴ M of* $Ag(phen)_2NO_3$ *and* $Ag(phen)_2(NO_3)_2$ *solutions in propylene carbonate for different rates of potential sweep* [$\mu = 0.1 - (C_2H_5)_4NNO_3$, $T = 298$ K]

v (V/min)	E_{pa} (V)	E_{pk} (V)	E_f^0 (V)
0.6	0.730	0.632	0.681
1.2	0.736	0.626	0.681
3.0	0.744	0.620	0.682
4.2	0.752	0.612	0.682
5.4	0.760	0.608	0.684
6.6	0.768	0.604	0.686

The rate of potential sweep ranged from 0.6 to 6.6 V/min. The curves obtained for the two solutions were identical and they are described in Table 5.

It follows from the results collected in Table 5 that we are dealing with a redox system quasi-reversible under the measurement conditions:

$$Ag(phen)_2^{2+} + e \rightleftharpoons Ag(phen)_2^{+}$$

Its formal potential (assuming $D_{ox} = D_{red}$) is equal to 0.681 ± 0.003 V vs. Ag/0.01 *M* $AgClO_4(PC)$. The potential of the Ag/0.01 *M* $AgClO_4(PC)$ electrode is 0.785 V relative to *NHE* in water [22], hence $E_{0.1}^0$ of the system under study is 1.466 V vs. *NHE*.

Discussion

Table 6 lists the β_2 values for AgL_2 type complexes in H_2O and in propylene carbonate.

Table 6. *Comparison of* AgL_2 *complex formation constant* (β_2) *in water and in propylene carbonate* ($\mu = 0.1$)

Ligand	$\log \beta_2$ (H_2O)	$\log \beta_2$ (*PC*)	Ref.
Pyridine	4.35	9.30	[26]
2,2′-Bipyridine	6.67	13.10	[26]
Phenanthroline	11.52	12.40	
Cl^-	5.3	20.86	[25]
Br^-	7.1	21.20	[7]
SCN^-	8.2	16.00	[7]

It is obvious that in a medium with higher dielectric constant ε, or with stronger ion-solvent interactions the values of complex formation constants β_2 should decrease. This is what happens in the case of acetonitrile [8], where one deals with strong Ag^+-*AN* interactions (*Pearson*'s soft acid—soft base).

Propylene carbonate has a comparable dielectric permittivity constant and donor number ($\varepsilon_{PC} = 65, DN_{PC} = 15.1$), considerably greater dipole moment ($\mu_{PC} = 4.98\ D$), and it is an aprotic solvent. *Popov*'s NMR studies [23] and Ag^+ ion solvation enthalpies [24] ($\Delta H^0_{\mathrm{sol}PC} = 96.3$ kcal/mol, $-\Delta H^0_{\mathrm{solH_2O}} = 96.0$ kcal/mol) point to slightly stronger cation-solvent interactions in the case of propylene carbonate. Thus, the differences in complex stabilities are probably due to different ligand-solvent interactions in H_2O and *PC*.

This is relatively easy to account for in the case of AgX_2^- type complexes. For X^- ions we have $-\Delta H^0_{\mathrm{solH_2O}} \gg -\Delta H^0_{\mathrm{sol}PC}$ because, by contrast with water, solvation in propylene carbonate takes place without the formation of hydrogen bridges. Hence the β_2 values of analogous complexes *PC* are markedly higher.

In the case of AgL_2^+ type complexes with uncharged ligand both *Debye*'s and *London*'s interactions of the latter with the solvent—although stornger than in the case of water—should be weaker and negligible in comparison with the $Ag^+ - S$ interactions. One could thus expect similar β_2 values in H_2O and in *PC*. Such is the case with the $Ag(phen)_2^+$ complex.

The considerable differences in the analogous β_2 values of $Ag(py)_2^+$ and $Ag(bipy)_2^+$ complexes [26] could be only accounted for in terms of anomaously strong *Keesom*'s interactions between propylene carbonate molecules which, with lower polarizability of pyridine and 2,2′-bipyridine molecules than in the case of 1,10-phenanthroline, doesn't lead to significant ligand solvation.

As could be expected, the E_f^0 potential of the $Ag(phen)_2^{2+}/Ag(phen)_2^+$ is different in the three solvents studied. On the other hand, by constrast with H_2O and *AN*, no disproportionation of the $Ag(phen)_2^{2+}$ complex was observed in propylene carbonate.

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