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Potentiometric Determination of Equilibrium Constants for Ag(I)—Pyridine, Ag(I)—2,2'-Bipyridine and Ag(I)—1,10-Phenanthroline Systems in Acetonitrile

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The composition and the complex formation constants of Ag(I) with pyridine, 2,2'-bipyridine, and 1,10-phenanthroline were determined by the potentiometric method. The measurement procedure can be reduced to the determination of the EMF of the concentration cell:

$$\mathrm{Ag}\,|\,c_1\,\mathrm{AgNO_3}(AN) + 0.1\,M\,(\mathrm{C_2H_5})_4\mathrm{NClO_4}(AN)\,\|\,0.1\,M\,(\mathrm{C_2H_5})_4\mathrm{NClO_4}(AN)\,\|\\ c_2\,\mathrm{AgNO_3}(AN) + x\,L(AN) + 0.1\,M\,(\mathrm{C_2H_5})_4\mathrm{NClO_4}(AN)\,|\,\mathrm{Ag}.$$

All complexes have coordination number 2. The solubility product for Ag(1,10-phenanthroline)$_2$NO$_3$ in acetonitrile was also determined. In all measurements the association of AgNO$_3$ was considered. Differences in the stability of analogous complexes in water and acetonitrile are discussed.

(Keywords: Acetonitrile; Formation constant of complexes; Precipitate; Potentiometry; Silver ions)

Potentiometrische Bestimmung der Gleichgewichtskonstanten in den Systemen Ag(I)—*Pyridin,* Ag(I)—*2,2'-Bipyridin und* Ag(I)—*1,10-Phenantrolin in Acetonitril*

Mit Hilfe der potentiometrischen Methode wurde die Zusammensetzung und Bildungskonstante der Komplexe Ag(I) mit Pyridin, 2,2'-Bipyridin und 1,10-Phenantrolin bestimmt. Die Messungsmethode kann man auf die EMK-Messung folgender Konzentrationskette zurückführen:

$$\mathrm{Ag}\,|\,c_1\,\mathrm{AgNO_3}(AN) + 0.1\,M\,(\mathrm{C_2H_5})_4\mathrm{NClO_4}(AN)\,\|\,0.1\,M\,(\mathrm{C_2H_5})_4\mathrm{NClO_4}(AN)\,\|\\ c_2\,\mathrm{AgNO_3}(AN) + x\,L(AN) + 0.1\,M\,(\mathrm{C_2H_5})_4\mathrm{NClO_4}(AN)\,|\,\mathrm{Ag}.$$

Alle Komplexe haben Koordinationszahl 2. Außerdem wurde der Wert des Löslichkeitsproduktes Ag(1,10-Phenantrolin)$_2$NO$_3$ im Acetonitril bestimmt. In allen Messungen wurde die Assoziation von $AgNO_3$ berücksichtigt. Es wurden weiterhin die Unterschiede in der Stabilität analoger Komplexe im Wasser und Acetonitril diskutiert.

Introduction

Potentiometric measurements in nonaqueous media require the stability of potential of the reference electrode in the given solvent. In the case of acetonitrile this condition is satisfied by the $Ag/AgNO_3$ 0.01 *M* electrode proposed by *Kolthoff* and *Kratochvil*[1,2], which is reversible and not very sensitive to possible impurities of the solvent, such as acrylonitrile, acetic acid, and ammonium acetate.

Experimental

Acetonitrile produced by VEB Laborchemie Apolda (GDR) was purified by the method of *Coetzee*[3] and the final distillation was carried out over P_2O_5. The fraction collected was the one whose boiling point at $p = 760$ mm Hg was 81.6 °C. Purification was carried out until a cut-off point was reached at $\lambda = 210$ nm and a specific conductivity of $2\text{–}3 \cdot 10^{-7}\ \text{ohm}^{-1}\ \text{cm}^{-1}$.

Analytically pure $AgNO_3$ was triply crystallized from *AN* and dried under vacuum at 120 °C to a constant weight.

Anhydrous $AgClO_4$ was obtained from analytically pure Ag_2CO_3 crystallized from water and then triply crystallized from *AN* followed by drying under vacuum at 70 °C to a constant weight.

$(C_2H_5)_4NClO_4$, obtained according to the procedure described by *Kolthoff*[4], was triply crystallized from *AN* and dried under vacuum at room temperature.

The EMF measurements were made with a V-541 voltmeter whose input resistance was 1 G ohm (accuracy ± 0.1 mV).

Methods and Results

Lack of precise values of activity coefficients of Ag^+ ions as a function of ionic strength in acetonitrile solution as well as divergent values for the formal potential of the $Ag \mid AgNO_3$ — 0.01 *M* (*AN*) electrode[5,6] made a straightforward potentiometric measurement of the Ag^+ concentration in acetonitrile impossible. In view of this it was decided to employ the measurement procedure described below.

The measurements were carried out in two systems.

In system I the measurement involved the dependence of EMF on $\log c_{AgNO_3}$

$$\text{I} \quad Ag \mid AgNO_3\,(0.01\,M)\,(AN) + (C_2H_5)_4NClO_4\,(0.1\,M)\,(AN) \parallel$$
$$(C_2H_5)_4NClO_4\,(0.1\,M)\,(AN) \parallel$$
$$c\,AgNO_3\,(AN) + (C_2H_5)_4NClO_4\,(0.1\,M)\,(AN) \mid Ag,$$

where c_{AgNO_3} was in the range of $10^{-6}\text{–}10^{-3}\ \text{mol/dm}^3$.

The electrolytic bridge was 0.1 *M* solution of $(C_2H_5)_4NClO_4\,(AN)$.

The ions making up $(C_2H_5)_4NClO_4$ have very similar mobilites. In the range of concentrations under study a straight line was obtained whose slope was

$$\frac{\partial \Delta E_1}{\partial \log c} = 58.1\,\mathrm{mV}.$$

In system II the equilibrium of the complexing process was investigated by determination of the EMF (ΔE_2) of the cell:

$$\begin{gathered}\mathrm{II}\quad \mathrm{Ag}\,|\,\mathrm{AgNO_3}\,(0.01\,M)\,(AN) + (\mathrm{C_2H_5})_4\mathrm{NClO_4}\,(0.1\,M)\,(AN)\,\| \\ (\mathrm{C_2H_5})_4\mathrm{NClO_4}\,(0.1\,M)\,(AN)\,\| \\ c\,\mathrm{AgNO_3}\,(AN) + x\,L(AN) + (\mathrm{C_2H_5})_4\mathrm{NClO_4}\,(0.1\,M)\,(AN)\,|\,\mathrm{Ag},\end{gathered}$$

where c_{AgNO_3} was in the range of 10^{-5}–$10^{-2}\,\mathrm{mol/dm^3}$, and $x\,L$ was the ligand concentration in the range of 10^{-3}–$5 \cdot 10^{-1}\,\mathrm{mol/dm^3}$. The stability of the potential of the $\mathrm{Ag}\,|\,\mathrm{AgNO_3}\,(0.01\,M)\,(AN) + (C_2H_5)_4NClO_4\,(0.1\,M)\,(AN)$ electrode was periodically checked in relation to the Fc^+/Fc electrode in acetonitrile.

Measurement carried out in this way can be reduced to measuring the EMF in the configuration:

$$\begin{gathered}\mathrm{III}\quad \mathrm{Ag}\,|\,c_1\,\mathrm{AgNO_3}\,(AN) + (\mathrm{C_2H_5})_4\mathrm{NClO_4}\,(0.1\,M)\,(AN)\,\| \\ (\mathrm{C_2H_5})_4\mathrm{NClO_4}\,(0.1\,M)\,(AN)\,\| \\ c_2\,\mathrm{AgNO_3}\,(AN) + x\,L(AN) + (\mathrm{C_2H_5})_4\mathrm{NClO_4}\,(0.1\,M)\,(AN)\,|\,\mathrm{Ag}.\end{gathered}$$

System III constitutes a concentration cell without a transferance whose EMF can be described by the equation:

$$\mathrm{EMF} = \Delta E = \Delta E_2 - \Delta E_1 = 0.0581 \log\frac{a_2}{a_1} \approx 0.0581 \log\frac{c_2}{c_1}, \qquad (1)$$

where the subscript "2" is related to the free Ag^+ ions in the solution of the complex under study.

Having measured the values of ΔE, the magnitude of c_2—denoted here by c_{exp}—was calculated from eq. (1). This procedure was employed for each initial concentration of $AgNO_3$ in configurations I and II. Potentiometric and conductometric measurements show that $AgNO_3$ in AN solution is partially associated, with the association constant extrapolated to $\sqrt{I} = 0$ is equal to 70.2 ± 0.5 (conductometric measurement[7]) or to 74 ± 5 (potentiometric[1]). Thus, the c_{exp} values obtained in this study represent the concentration of free Ag^+ ions in equilibrium after the complexing and association in $AgNO_3$. The concentration of Ag^+ ions related to complexing equilibrium can be

Table 1. *Results of measurements of the conditional association constant for* $AgNO_3$ *in acetonitrile* [$I = 0.1$ — $(C_2H_5)_4NClO_4$]

$c \cdot 10^3$ Ag^+ mol/dm^3	ΔEMF mV	$c_{exp} \cdot 10^3$ Ag^+ mol/dm^3	$c_{as} \cdot 10^3$ Ag^+ mol/dm^3	K_{as}
10	− 10.3	6.6484	3.3515	75.82
5	− 6.5	3.8645	1.1355	76.00
2	− 3.1	1.7688	0.2312	73.90
1	− 1.7	0.9348	0.0652	74.60

obtained from a given association constant for $AgNO_3$ under the conditions of measurement.

Determination of the Association Constant $K_{as\,0.1}$ *for* $AgNO_3$ *in Acetonitrile*

Contrary to $AgNO_3$, $AgClO_4$ is completely dissociated in acetonitrile[7], so it is possible to determine potentiometrically the conditions—dependent association constant of $AgNO_3$ in $(C_2H_5)_4NClO_4$ solution in *AN* of $I = 0.1$ using $AgClO_4$ as standard for the Ag^+ ions concentration. The EMF measurements were carried out in the system:

$$\text{IV}\quad \mathrm{Ag}\,|\,c\,\mathrm{AgNO_3}\,(AN) + 0.1\,M\,\mathrm{(C_2H_5)_4NClO_4}\,(AN)\,\|\\ 0.1\,M\,\mathrm{(C_2H_5)_4NClO_4}\,(AN)\,\|\\ c\,\mathrm{AgClO_4}\,(AN) + 0.1\,M\,\mathrm{(C_2H_5)_4NClO_4}\,(AN)\,|\,\mathrm{Ag},$$

where $c = 10^{-3}$–10^{-2} mol/dm^3.

The obtained results are presented in Table 1.

The value of the association constant $K_{as\,0.1} = 75 \pm 3$ is in a good agreement with the values obtained by *Yeager*[7].

Determination of the Composition and Formation Constants of Ag(I) *Complexes*

In all cases the compositions of the complexes were determined from the dependence

$$\left(\frac{\partial \Delta E}{\partial \log c_L}\right)_{c_0} = \frac{n\,RT}{z\,F}$$

by analogy with the corresponding measurements in aqueous solutions. For small values of c_0 (negligible association of $AgNO_3$) this dependence is linear. The coordination number *n* for all ligands under investigation ranged from 1.90 to 2.05.

Table 2. *Results of measurements of the conditional complex formation constant for* Ag(I)—*pyridine* $[\mathrm{Ag}(py)_2^+]$ *in acetonitrile* $[I = 0.1$ — $(C_2H_5)_4NClO_4]$

$c_0 \cdot 10^4$ mol/dm^3	c_L^0 mol/dm^3	ΔE mV	$c_{\mathrm{exp}} \cdot 10^4$ mol/dm^3	$c_{\mathrm{as}} \cdot 10^4$ mol/dm^3	$c_{\mathrm{compl}} \cdot 10^4$ mol/dm^3	$\beta \cdot 10^{-3}$
0.5	$0.5 \cdot 10^{-2}$	− 51,7	0.06595	0.000247	0.4338	2.62
1.07		− 52.0	0.13936	0.00112	0.9295	2.67
5.33		− 52.0	0.69846	0.02792	4.6036	2.63
10.9		− 53.0	1.37121	0.12096	9.4078	2.72
51.2		− 52.5	6.54067	2.5116	42.1477	2.69
100		− 51.3	13.368	10.026	76.606	2.72
0.5	$1 \cdot 10^{-2}$	− 84.3	0.01836	0.000068	0.48157	2.62
1.07		− 84.1	0.03956	0.000317	1.03	2.59
5.33		− 85.1	0.19066	0.00762	5.1317	2.64
10.9		− 84.7	0.39543	0.03233	10.472	2.56
51.2		− 87.6	1.6507	0.63386	48.91	2.63
100		− 89.3	3.0109	2.258	94.73	2.72
0.5	$5 \cdot 10^{-1}$	− 166.1	0.0007419	0.0000028	0.49925	2.68
1.07		− 166.3	0.001574	0.0000059	1.06840	2.71
5.33		− 165.8	0.00804	0.0000302	5.3219	2.64
10.9		− 165.5	0.0166	0.001358	10.882	2.45
51.2		− 171.0	0.06264	0.02405	51.113	2.53
100		− 176.9	0.09691	0.07268	99.83	2.56

$\bar{\beta}_{0.1} = (2.65 \pm 0.25) \cdot 10^3$.

In the case of a mononuclear complex with coordination number 2 (ion of form $\mathrm{Ag}L_2^+$) the constant of complex formation for $c_L^0 \gg n\, c_0$ and $c_L \approx c_L^0$ is given by the expression:

$$\beta_2 = \frac{c_0 - c_{\mathrm{exp}}\left(1 + \dfrac{K_{\mathrm{as}}\, c_0}{1 + K_{\mathrm{as}}\, c_{\mathrm{exp}}}\right)}{c_{\mathrm{exp}}\left(1 + \dfrac{K_{\mathrm{as}}\, c_0}{1 + K_{\mathrm{as}}\, c_{\mathrm{exp}}}\right)(c_L^0)^2} \tag{2}$$

Under the conditions of the measurement $K_{\mathrm{as}} = 75$ and $K_{\mathrm{as}}\, c_{\mathrm{exp}} \ll 1$, hence eq. (2) becomes simplified to:

$$\beta_2 = \frac{c_0 - c_{\mathrm{exp}}\,(1 + K_{\mathrm{as}}\, c_0)}{c_{\mathrm{exp}}\,(1 + K_{\mathrm{as}}\, c_0)\,(c_L^0)^2} \tag{3}$$

where c_L^0 is the initial concentration of the ligand.

Table 3. *Results of measurements of the conditional complex formation constant for* Ag(I)—*2,2-bipyridine* [Ag(*bipy*)$_2^+$] *in acetonitrile* [$I = 0.1$ — $(C_2H_5)_4NClO_4$]

$c_0 \cdot 10^4$ mol/dm^3	c_L^0 mol/dm^3	ΔE mV	$c_{exp} \cdot 10^7$ mol/dm^3	$c_{as} \cdot 10^7$ mol/dm^3	$c_{compl} \cdot 10^4$ mol/dm^3	$\beta \cdot 10^{-5}$
0.5	$5 \cdot 10^{-2}$	– 161.1	0.9027	0.00338	0.4991	2.20
1.07		– 160.6	1.968	0.0158	1.068	2.16
5.33		– 161.4	9.559	0.382	5.32	2.14
10.9		– 162.0	19.06	1.558	10.88	2.11
51.2		– 168.9	68.02	26.12	51.106	2.17
100		– 179.3	88.20	66.15	84.565	2.19
0.5	10^{-1}	– 197.0	0.2267	0.0008	0.4998	2.20
1.07		– 197.4	0.4646	0.0037	1.0695	2.28
5.33		– 196.8	2.3840	0.0953	5.3275	2.15
10.9		– 197.3	4.7735	0.3900	10.8950	2.11
51.2		– 204.0	17.1000	6.590	51.1976	2.16
100		– 209.7	26.766	20.070	99.9532	2.13
0.5	$5 \cdot 10^{-1}$	– 278.5	0.009	0.00003	4.99991	2.21
1.07		– 278.2	0.0195	0.00015	1.069998	2.18
5.33		– 278.5	0.0967	0.00387	5.3299	2.12
10.9		– 279.3	0.1938	0.0156	10.8998	2.11
51.2		– 285.7	0.6964	0.2674	51.199	2.12
100		– 292.1	1.056	0.7923	99.998	2.16

$\bar{\beta}_{0.1} = (2.16 \pm 0.2) \cdot 10^5$.

The results of the measurements and the values of the formation constants for the complexes under investigation are collected in Tables 2–4.

Determination of the Solubility Product for Ag(*phen*)$_2$NO$_3$ *in Acetonitrile*

During the determination of the complex formation constant β_2 for Ag(*phen*)$_2^+$ (*phen* = 1,10-phenanthroline), precipitation of Ag(*phen*)$_2$NO$_3$ was observed at higher reagent concentrations, while no such effect was observed when solutions of Ag$^+$ ions in the form of AgClO$_4$ were used.

Fig. 1 presents a typical dependences of the EMF for the system on the concentration of added AgNO$_3$ for a given 1,10-phenanthroline concentration.

Three regions can be distinguished in the plots of Fig. 1 (*1, 2*): region I which illustrates the equilibrium of the complexing process [for this range of concentrations the composition and complex formation constant for Ag(*phen*)$_2^+$ were determined], region II which illustrates the

Table 4. *Results of measurements of the conditional complex formation constant for* Ag(I)—*1,10-phenanthroline* [Ag(*phen*)$_2^+$] *in acetonitrile* [$I = 0.1$ — $(C_2H_5)_4NClO_4$]

$c_0 \cdot 10^4$ mol/dm³	c_L^0 mol/dm³	ΔE mV	$c_{exp} \cdot 10^{12}$ mol/dm³	$c_{as} \cdot 10^{12}$ mol/dm³	$c_{compl} \cdot 10^4$ mol/dm³	$\beta \cdot 10^{-9}$
0.1	$2.71 \cdot 10^{-3}$	−275.9	191.4	0.143	0.1	7.19
	5.10^{-3}	−308.0	543.0	0.402	0.1	7.4
0.312	$2.71 \cdot 10^{-3}$	−276.1	597.38	1.40	0.312	7.4
	$5 \cdot 10^{-3}$	−308.9	162.98	3.81	0.312	7.63
0.5	$2.71 \cdot 10^{-3}$	−275.0	998	3.7	0.5	7.25
	$5 \cdot 10^{-3}$	−306.1	294	1.1	0.5	7.35
	$5 \cdot 10^{-2}$	−425.0	2.723	0.0102	0.5	7.30
	$1 \cdot 10^{-1}$	−460.3	0.6867	0.0026	0.5	7.25
	$5 \cdot 10^{-1}$	−542.1	0.02723	0.0001	0.5	7.30

$\beta_{0.1} = (7.34 \pm 0.5) \cdot 10^9$.

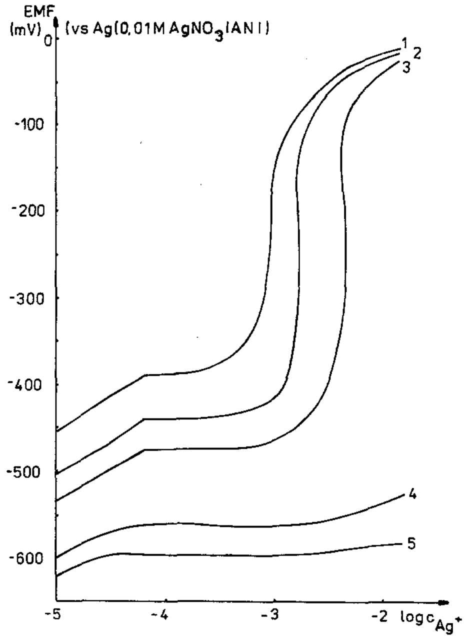

Fig. 1. Dependence of EMF for Ag(I)—1,10-phenanthroline in acetonitrile as a function of $AgNO_3$ concentration for different ligand concentrations [$I = 0.1$ — $(C_2H_5)_4NClO_4$]. *1* $2 \cdot 10^{-3}$ mole/dm³, *2* $5 \cdot 10^{-3}$ mole/dm³, *3* $1 \cdot 10^{-2}$ mole/dm³, *4* $5 \cdot 10^{-2}$ mole/dm³, *5* $1 \cdot 10^{-1}$ mole/dm³

equilibrium between the complex forming in the solution and its solid and region III which represents Ag^+ ions in equilibrium with the solution and solid of the complex salt. The solubility product of the complex salt can be determined by considering the equilibria characterising the second region and regarding the association of $AgNO_3$.

In the case of precipitation of the complex $Ag(phen)_2NO_3$ salt, the equilibria of the second region can be described in the following way:

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

$$Ag(phen)_2^+ + NO_3^- \overset{K_{so}}{\rightleftharpoons} Ag(phen)_2NO_3 \qquad \text{II}$$

$$Ag^+ + NO_3^- \overset{K_{as}}{\rightleftharpoons} AgNO_3 \qquad \text{III}$$

The solubility product for the $Ag(phen)_2NO_3$ is described by the expression:

$$K_{so} = c_{exp}^2 \left[\frac{1 + K_{as}\,c_{exp}}{1 - K_{as}\,c_{exp}\,\beta_2\,(c_L^0 + 2\,x_{exp} - 2\,c_0)^2} \right]^2 \cdot$$
$$[1 + \beta_2\,(c_L^0 + 2\,c_{exp} - 2\,c_0)^2]^2 \qquad (4)$$

Under the conditions of the measurement [$K_{as} = 75$, c_{exp} in the given region 10^{-9}–10^{-10} mol/dm^3, $\beta_2\,Ag(phen)_2^+ = 7.34 \cdot 10^9$ and c_{phen}^0 10^{-3}–10^{-1} mol/dm^3]

$$K_{as}\,c_{exp} \ll 1, \quad c_{exp} \ll c_0$$

$$K_{as}\,c_{exp}\,\beta_2\,(c_L^0 - 2\,c_0 + 2\,c_{exp})^2 \ll 1$$

and

$$1 + \beta_2\,(c_L^0 - 2\,c_0 + 2\,c_{exp})^2 \approx \beta_2\,(c_L^0 - 2\,c_0)^2.$$

Thus, expression (4) reduces to a simple equation of the form

$$K_{so} = c_{exp}^2\,\beta_2^2\,(c_L^0 - 2\,c_0)^4 \qquad (5)$$

The results of measurements leading to the determination of K_{so} and the values of K_{so} are presented in Table 5.

The solubility product of the complex salt for $Ag(phen)_2NO_3$ in acetonitrile obtained in this study is:

$$K_{so} = (4.02 \pm 0.45) \cdot 10^{-9}$$

Table 5. *Values of the conditional constant of* Ag(*phen*)$_2$NO$_3$ *precipitate formation* — K_{so} [$I = 0.1$ — (C$_2$H$_5$)$_4$NClO$_4$]

$c_0 \cdot 10^4$ mol/dm^3	c_L^0 mol/dm^3	EMF$_{exp}$ mV	ΔE mV	$c_{exp} \cdot 10^{11}$ mol/dm^3	$K_{so} \cdot 10^9$
1.23	$2 \cdot 10^{-3}$	− 387.7	− 274.7	276.8	3.91
2.51		− 378.8	− 284.0	393.5	4.22
5.44		− 353.3	− 279.1	1032	3.98
0.663	$5 \cdot 10^{-3}$	− 438.9	− 309.9	37.87	4.37
1.23		− 438.5	− 325.5	38.26	4.03
2.51		− 463.3	− 341.5	41.89	3.89
5.44		− 428.7	− 354.5	54.68	3.79
11.0		− 420.7	− 354.4	111.0	4.10
0.663	10^{-2}	− 476.7	− 347.7	8.685	3.88
1.23		− 475.9	− 362.9	8.912	3.89
2.51		− 473.3	− 378.5	9.912	4.33
5.44		− 469.9	− 395.7	10.98	4.13
11.0		− 463.6	− 407.3	14.13	3.98
0.663	$5 \cdot 10^{-2}$	− 559.0	− 430.0	0.3518	4.12
1.23		− 544.4	− 431.4	0.3331	3.68
2.51		− 558.9	− 464.1	0.3531	4.05
5.44		− 557.7	− 483.5	0.3591	3.98
11.0		− 557.0	− 500.7	0.3715	3.88
51.2		− 546.8	− 529.8	0.5566	4.17
0.663	10^{-1}	− 594.4	− 465.4	0.08859	4.24
1.23		− 594.4	− 481.4	0.08812	4.17
2.51		− 594.6	− 499.8	0.08787	4.10
5.44		− 594.1	− 519.9	0.08697	3.91
11.0		− 593.3	− 537.0	0.09034	4.03
51.2		− 585.3	− 572.3	0.1063	3.97
100		− 583.5	− 583.5	0.1342	3.98

$\bar{K}_{so\,(0.1)} = (4.02 \pm 0.45) \cdot 10^{-9}$.

Table 6. *Conditional complex formation constants for* AgL_2^+ *in* H$_2$O *and AN* ($I = 0.1$)

$\log \beta_{(H_2O)}$	Ligand	$\log \beta_{(AN)}$	$\Delta \log \beta$
4.35[8]	pyridine	3.42	0.97
6.67[9]	2,2-bipyridine	5.33	1,34
12.07[10]	1.10-phenanthroline	9.87	2.20
11.52*[11]			1.65

* $\beta_{0.1}$ in 0.1 M (C$_2$H$_5$)$_4$NClO$_4$.

Discussion

The values of the complex formation constants for the studied complexes $AgL_2 - \log\beta$ in *AN* and the values of $\log\beta$ for these complexes in water are collected in Table 6.

The stability of the investigated Ag(I) complexes in acetonitrile is smaller than in water. This is obvious from the fact that relatively stable $Ag(CH_3CN)_2^+$ complexes of $\beta = 2.98$ are formed in *AN*; for the $Ag(H_2O)^+$ complexes $\beta = 0.13$[6].

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