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Silver Complexes with I^-, Br^- and SCN^- in Sulfolane

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The solubility product constants of silver bromide(I), iodide(II), and thiocyanate(III) and the over-all formation constants β of $Ag_nX_m^{(m-n)-}$ *(X = Br, I, SCN) complexes in sulfolane at 30°, have been calculated from potentiometric titrations. At ionic strength* $\mu = 0.1$ *the stoichiometric solubility product constants were:* 6.6×10^{-19} *(I),* 3.3×10^{-19} *(II),* 5.4×10^{-17} *(III). In the range of complexing agent concentrations explored, only one complex has been found for* Br^- *(*$AgBr_2^-$*,* $\beta=2.1\times10^{19}$*), only one complex for* I^- *(*$Ag_3I_4^-$*,* $\beta=3.3\times10^{56}$*) and only one complex for* SCN^- *(*$Ag(SCN)_2^-$*,* $\beta=1.1\times10^{16}$*). The above formulas of the complex ions have been also confirmed by conductometric titrations.*

Introduction

In the course of previous experiments[1] we have noticed that when a silver wire covered with silver halide is dipped in a solution of halide in sulfolane, the AgX deposit is dissolved. This fact may be explained in terms of complex formation between silver and halide ions in this solvent.

The present work was undertaken to determine the solubility of silver bromide, iodide and thiocyanate and the stability of the $Ag_nX_m^{(m-n)-}$ complexes in sulfolane, as well as to study the titration of silver ion in this solvent.

Experimental Section

Materials. Sulfolane (tetramethylensulfone), kindly supplied by the Shell Italiana, was distilled from solid sodium hydroxide under reduced pressure (10^{-4} Torr) until its conductivity decreased to 2.0×10^{-8} omh^{-1} cm^{-1}.[2]

Silver perchlorate was recrystallized from conductivity water and dried at 110° under reduced pressure. Tetraethylammonium bromide (B.D.H.) was recrystallized three times from acetonitrile, washed with ether, and dried in vacuum at 30°. Reagent-grade potassium iodide and bromide were recrystallized three times from ethanol-conductivity water and dried for 10 hrs. over P_2O_5 at 90° under reduced pressure. Fisher Certified A.C.S. potassium thiocyanate was recrystallized from conductivity water and dried for 40 hrs. at 60° under reduced pressure. Tetraethylammonium perchlorate was prepared by adding silver perchlorate to tetraethylammonium iodide in water; the silver perchlorate addition was controlled potentiometrically. After filtration of silver iodide the solution was evaporated; the tetraethylammonium perchlorate was filtered, recrystallized from conductivity water and dried in vacuum at 50°.

Potentiometric and Conductometric Measurements. The titrations were performed both by potentiometric and conductometric techniques.

Great care was taken during the titrations in order to avoid air moisture.

The indicator electrode was a spongy silver wire, prepared according the method described by Jones and Dole.[3] A microburet, calibrated to 0.01 ml. was fitted in the titration cell. All potentials were measured against a water saturated calomel electrode connected to the cell through NH_4NO_3 agar bridge. In order to prevent diffusion of water from the salt bridge into the $AgClO_4$ sulfolane solution during the measurements, a modified Kolthoff and Coetzee[4] cell was used.

The differential potentiometric method described by Mac Innes and Dole[5] has been also used in some measurements. This method has the advantage of avoiding the use of a aqueous reference electrode and of a salt bridge.

In the conductometric titrations a cell with smooth platinum electrodes was used and the solution was stirred magnetically. Both the titration cell and the microburet were kept at 30°±0.2 using an air thermostat.

For the determination of the solubility constants and the over-all formation constants of the complexes $Ag_nX_m^{(m-n)-}$, the initial concentration of silver perchlorate ranged from about 10^{-3} to 10^{-4} *M*. In each experiment the ionic strength was maintained at $\mu = 0.1$ by adding $(C_2H_5)_4NClO_4$.

Treatment of the Data. In Figure 1, the points «A» correspond to the precipitate being completely dissolved. After these points, since the concentration of free silver ions (as calculated from potentiometric readings) is very small, it may be assumed that:

$$[Ag_nX_m^{(m-n)-}] = [Ag^+_{total}]/n \qquad (1)$$

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[1] M. Della Monica, U. Lamanna, and L. Senatore, *J. Phys. Chem.*, *72*, 2124 (1968).

[2] R. L. Burwell and C. H. Langford, *J. Am. Chem. Soc.*, *81*, 3799 (1959).

[3] G. Jones and M. Dole, *J. Am. Chem. Soc.*, *51*, 1073 (1929).

[4] I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, *79*, 870 (1957).

[5] D. A. Mac Innes and M. Dole, *J. Am. Chem. Soc.*, *51*, 1119 (1929).

where $[Ag^+_{total}]$ is the initial concentration of silver ions corrected for the volume of titrant added. The concentration of free $[X^-]$ ions may be obtained from the following relationship:

$$[X^-]=[X^-_{total}]-\frac{m}{n}[Ag^+_{total}] \tag{2}$$

The values of the β constants are given by

$$\beta=[Ag_nX_m{}^{(m-n)-}]/[Ag^+]^n\cdot[X^-]^m \tag{3}$$

for $AgBr_2^-$, $Ag_3I_4^-$, and $Ag(SCN)_2^-$ complexes. The values of β were then calculated from several points beyond that corresponding to all the precipitate being dissolved (beyond the points «A»).

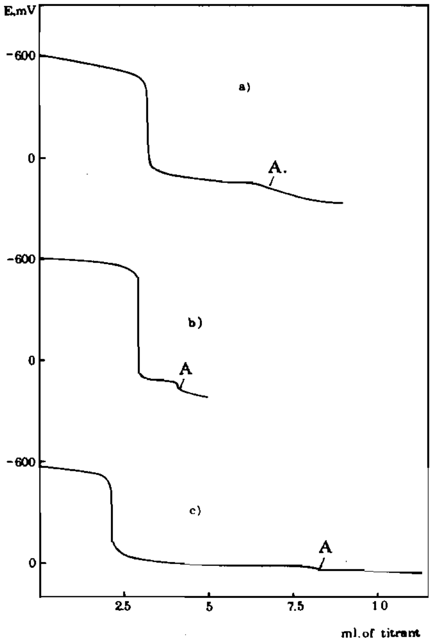

Figure 1. Potentiometric titration curves in sulfolane at 30°C; [a] Silver perchlorate solution 5×10^{-3} N titrated with Et_4NBr 5×10^{-2} N; [b] Silver perchlorate solution 5×10^{-3} N titrated with KI 5×10^{-2} N; [c] Silver perchlorate solution 3×10^{-3} N titrated with KSCN 5×10^{-2} N. All the experiments were performed at ionic strength maintained at $\mu=0.1$ with $(C_2H_5)_4NClO_4$.

The solubility products ($K_{sp}=[Ag^+]\cdot[X^-]$) for AgBr, AgI and Ag(SCN) salts were calculated from potentiometric curve in the region between the equivalence point and the point corresponding to the silver salt being completely dissolved. The silver ion concentration at each point was evaluated from the e.m.f. reading before the addition of X^- ion, through the use of the Nernst's equation.[6] Owing to the presence of the complex ions, the concentration of X^- ion was obtained in this region by the following relationships:

$$\frac{[Ag_nX_m{}^{(m-n)-}]}{[X^-]^m}=\beta[Ag^+]^n \tag{4}$$

and

$$[M^+]+[Ag^+]=(m-n)[Ag_nX_m{}^{(m-n)-}]+[X^-] \tag{5}$$

where $[M^+]$ is the amount (*M*) of the cation of the salt added after the equivalence point.

Results

The accuracy of silver determinations in sulfolane by potentiometric titrations is shown in Table I.

Starting from the equivalence point the potential readings of three runs for the precipitation of silver ion by bromide, iodide and thiocyanate ions are summarized in Tables II, III, and IV. In the same tables the values of the solubility product constants (K_{sp}) as well as the over-all formation constants (β), are reported.

Table I. Accuracy of silver determination in sulfolane by potentiometric measurements

Salt	Titrant	Taken mg	Found mg	Accuracy %
Silver perchlorate	potassium iodide	6.220	6.201	99.7
		31.15	31.21	100.2
		60.53	60.41	99.8
Silver perchlorate	tetraethyl-ammonium bromide	5.934	5.916	99.7
		32.76	32.79	100.1
		64.15	63.96	99.7
Silver perchlorate	potassium thiocyanate	7.159	7.130	99.6
		21.14	21.20	100.3
		30.85	30.82	99.9
		61.18	61.42	100.4

Discussion

Figure 2-a shows the differential potentiometric titration curve of silver perchlorate by potassium iodide. The first peak occurs when one equivalent of I^- has been added to one equivalent of Ag^+. After

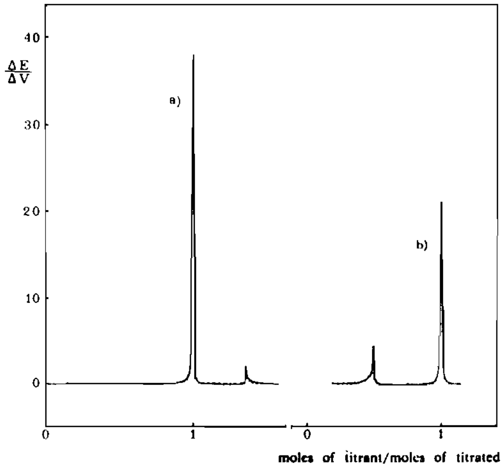

Figure 2. Differential potentiometric titration curves: [a] Silver perchlorate solution 0.1 N. titrated with KI 1 N; [b] Potassium bromide solution 1.2×10^{-3} N titrated with $AgClO_4$ 4×10^{-2} N. In abscissa the ratio « moles of titrant/moles of titrated » is reported.

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(6) The validity of Nernst's equation for the Ag/Ag^+ electrode in this solvent has been verified for the range of silver ions concentrations between $10^{-1}\div10^{-5}$ *M*.

Table II. Experimental data of the titration of $AgClO_4$ with $(C_2H_5)_4NBr$. $c_{AgCl_4}=5.269\times10^{-3}\,M$; $c_{(C_2H_5)_4NBr}=5.628\times10^{-2}\,M$

E, mV (vs. S.C.E.)	c_{Ag^+} (M)	c_{Br^-} (M)	$c_{AgBr_2^-}$ (M)	$K_{sp}\times10^{+19}$	$\beta\times10^{-19}$
−605.5	5.269×10^{-3}				
−210.0	1.40×10^{-9}	2.02×10^{-10}	1.20×10^{-9}	(2.8)	—
+ 63.0	4.05×10^{-14}	1.74×10^{-5}	2.57×10^{-4}	7.0	—
+ 83.5	1.85×10^{-14}	3.70×10^{-5}	5.33×10^{-4}	6.8	—
+104.5	8.28×10^{-15}	7.85×10^{-5}	1.07×10^{-3}	6.5	—
+117.7	5.00×10^{-15}	1.28×10^{-4}	1.73×10^{-3}	6.4	—
+121.2	4.37×10^{-15}	1.61×10^{-4}	2.39×10^{-3}	7.0	—
+127.4	2.71×10^{-15}	2.29×10^{-4}	3.00×10^{-3}	6.2	—
				6.6	
+189.5	3.20×10^{-16}	7.78×10^{-4}	4.38×10^{-3}		2.3
+201.0	2.06×10^{-16}	1.05×10^{-3}	4.36×10^{-3}		1.9
+212.5	1.33×10^{-16}	1.31×10^{-3}	4.33×10^{-3}		1.9
+232.5	6.17×10^{-17}	1.83×10^{-3}	4.29×10^{-3}		2.1
+240.0	4.63×10^{-17}	2.09×10^{-3}	4.27×10^{-3}		2.1
+255.5	2.56×10^{-17}	2.72×10^{-3}	4.22×10^{-3}		2.2
+267.0	1.65×10^{-17}	3.34×10^{-3}	4.17×10^{-3}		2.3
					2.1

Table III. Experimental data of the titration of $AgClO_4$ with KI. $c_{AgClO_4}=5.269\times10^{-3}\,M$; $c_{KI}=5.266\times10^{-2}\,M$

E, mV (vs. S.C.E.)	c_{Ag^+} (M)	c_{I^-} (M)	$c_{Ag_3I_4^-}$ (M)	$K_{sp}\times10^{+19}$	$\beta\times10^{-56}$
−606.0	5.269×10^{-3}				
−186.0	5.49×10^{-10}	2.70×10^{-10}	2.81×10^{-10}	(1.5)	—
+114.8	5.49×10^{-15}	5.53×10^{-5}	5.11×10^{-4}	3.0	—
+118.5	4.75×10^{-15}	6.57×10^{-5}	6.60×10^{-4}	3.1	—
+121.1	4.31×10^{-15}	7.45×10^{-5}	8.10×10^{-4}	3.2	—
+123.0	4.01×10^{-15}	8.20×10^{-5}	9.59×10^{-4}	3.3	—
+125.1	3.70×10^{-15}	9.06×10^{-5}	1.12×10^{-3}	3.4	—
+127.0	3.43×10^{-15}	9.85×10^{-5}	1.26×10^{-3}	3.4	—
+128.5	3.25×10^{-15}	1.06×10^{-4}	1.40×10^{-3}	3.4	—
				3.3	
+168.8	6.93×10^{-16}	3.47×10^{-4}	1.54×10^{-3}		3.2
+182.5	4.10×10^{-16}	5.81×10^{-4}	1.53×10^{-3}		2.0
+197.4	2.32×10^{-16}	7.35×10^{-4}	1.53×10^{-3}		4.2
+209.5	1.46×10^{-16}	1.04×10^{-3}	1.52×10^{-3}		4.1
+223.0	8.70×10^{-17}	1.65×10^{-3}	1.50×10^{-3}		3.1
					3.3

Table IV. Experimental data of the titration of $AgClO_4$ with KSCN. $c_{AgClO_4}=3.673\times10^{-3}\,M$; $c_{KSCN}=5.245\times10^{-2}\,M$

E, mV (vs. S.C.E.)	c_{Ag^+} (M)	c_{SCN^-} (M)	$c_{Ag(SCN)_2^-}$ (M)	$K_{sp}\times10^{+17}$	$\beta\times10^{-16}$
−576.2	3.673×10^{-3}				
−330.0	9.08×10^{-9}	5.80×10^{-9}	3.45×10^{-9}	5.3	—
0.0	2.96×10^{-14}	1.77×10^{-3}	1.05×10^{-3}	5.2	—
+ 2.5	2.69×10^{-14}	1.95×10^{-3}	1.16×10^{-3}	5.2	—
+ 3.0	2.64×10^{-14}	2.03×10^{-3}	1.23×10^{-3}	5.4	—
+ 9.0	2.10×10^{-14}	2.61×10^{-3}	1.62×10^{-3}	5.5	—
+ 16.0	1.61×10^{-14}	3.42×10^{-3}	2.13×10^{-3}	5.5	—
+ 19.5	1.40×10^{-14}	4.10×10^{-3}	2.66×10^{-3}	5.7	—
+ 25.0	1.14×10^{-14}	4.89×10^{-3}	3.08×10^{-3}	5.6	—
				5.4	
+ 37.0	7.19×10^{-15}	5.90×10^{-3}	2.86×10^{-3}		1.1
+ 43.5	5.60×10^{-15}	6.83×10^{-3}	2.80×10^{-3}		1.1
+ 49.5	4.45×10^{-15}	7.40×10^{-3}	2.77×10^{-3}		1.1
+ 54.0	3.75×10^{-15}	7.94×10^{-3}	2.73×10^{-3}		1.2
+ 59.5	3.04×10^{-15}	8.80×10^{-3}	2.68×10^{-3}		1.1
					1.1

this point by addition of iodide ions the silver iodide precipitate dissolves until the second peak is reached. The ratio of the amount of titrant added at the first peak to that added at the second peak is 1.33. This means that the formula of the complex ion is $Ag_3I_4^-$.

Figure 2-b shows the differential potentiometric curve for the titration of Ag^+ by potassium bromide. In this case the silver perchlorate was added to the potassium bromide solution; the first peak occurs when half equivalent of silver ion has been added to one of Br^-; after this point silver bromide begins to precipitate. The second peak occurs when one equivalent of Ag^+ has been added to one equivalent of bromide ion; so that the formula of the complex ion is $AgBr_2^-$.

At higher concentrations of halide ion, probably more than one complex is formed. Nevertheless, in the concentration range used in this work, the constancy of the values shows clearly that only one complex is present. It should be noted that for the calculations of the constants reported in Tables II, III, and IV no correction has been made for the presence of ion-pair species, because of the lack of the appropriate data in this solvent. Nevertheless, these corrections should be small, since the ion-pair formation constants for the various equilibria in solution *e.g.* ($(C_2H_5)_4N^+$, ClO_4^-), ($(C_2H_5)_4N^+$, Br^-), and ($(C_2H_5)_4N^+$, I^-) probably do not exceed the value of $10\,M^{-1}$.[7]

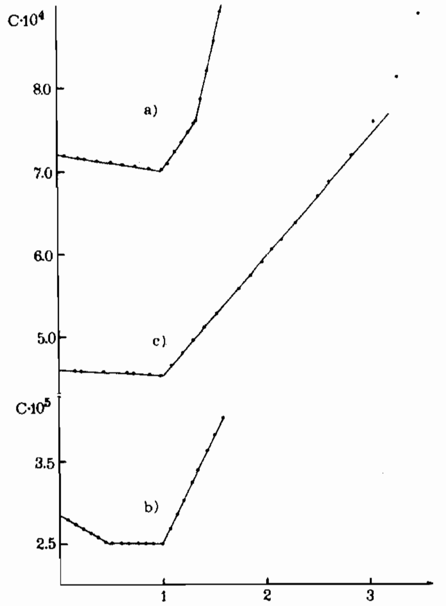

Figure 3. Conductometric titration curves in sulfolane at 30°C: ^{a} Silver perchlorate solution 0.1 N titrated with KI 1 N; ^{b} Potassium bromide solution 2.5×10^{-3} N titrated with $AgClO_4$ 4×10^{-2} N; ^{c} Silver perchlorate solution 7×10^{-2} N titrated with KSCN 1 N. In abscissa the ratio « moles of titrant/moles of titrated » is reported.

In the case of $AgClO_4$ titrated with KI, the conductometric curve (Figure 3a) presents two inflexions: the first one at the equivalence point and the second when the precipitate of silver iodide is completely dissolved. The ratio between the moles of the KI added at the two points is 1.33. This is in accord with the formula for the complex ion $Ag_3I_4^-$ which was obtained from the potentiometric results. As may be seen from Figure 3a, until the equivalence pont is reached the conductivity slowly decreases because the silver ions are replaced by slower potassium ions.[8] After the equivalence point, the complex ions are formed according to the reaction:

$$3AgI + K^+ + I^- = Ag_3I_4^- + K^+$$

and the conductance of the solution increases. Once all the precipitate is dissolved, the further addition of KI causes a sharper increase of the conductance. The different slopes of the curve after the equivalence point means that the mobility of complex ions is lower than that of I^- ions. In addition, since the conductance changes sharply when 1.33 equivalents of I^- ions are added for 1 equivalent of Ag^+ ions, it may be stated that the complex ion is very stable.

Also in the case of KBr titrated with $AgClO_4$ the conductometric titration curve (Figure 3b), presents two inflexions for a ratio $[Ag^+]/[Br^-]$ equal to 0.5 and 1 respectively. From this the formula of the complex appears to be $AgBr_2^-$ which agrees with the potentiometric results.

In the case of the titration of silver with SCN^- the formation of complex ions after the equivalence point does not affects the shape of the potentiometric and conductometric curve as in the case of the Br^- and I^- ions. The precipitate is completely dissolved when more than 3 equivalents of SCN^- ions have been added to one of Ag^+.

Tentatively the simultaneous presence of complexes such as $Ag(SCN)_m^{(m-1)-}$ ($m=2, 3, 4$) have been assumed and the value of the solubility product constant has been calculated in the range between the complete precipitation and the complete dissolution of the silver ion. These values are constant (Table IV) only when one complex, $Ag(SCN)_2^-$, is assumed to be present in solution.

The conductometric titration curve shows only one inflexion at the equivalence point. The value of the over-all formation constant β indicates that, the Ag(SCN) precipitate will be completely dissolved only in a large excess of SCN^- ions. This explains the lack of a sharp inflexion in the conductance curve when 2 equivalents of KSCN have been added to 1 equivalent of Ag^+. After the equivalence point the conductance increase of the solution is due both to the complex ions and the SCN^- ions in concentration almost equal (see Table IV).

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(7) M. Della Monica and U. Lamanna, *J. Phys. Chem.*, in press; R. Fernandez-Prini and J. E. Prue, *Trans. Faraday Soc.*, *61*, 1257 (1966).

(8) Ref. No. 1. From the data of Table II, a $\lambda_{oAg^+}=4.75$ can be calculated. The λ_o^+ for K^+ ion is 4.05.