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Ionic Solvation

Part 4.¹—Copper(1) Solvation. Disproportionation and Halide-complex Formation in Propylene Carbonate

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Potentiometric measurements have been obtained in order to examine the thermodynamic stability of copper(I) species and to study halide-complex formation in propylene carbonate in a 0.1 mol dm⁻³ tetraethylammonium perchlorate medium at 25 °C. A value of $10^{-3.44}$ dm³ mol⁻¹ has been found for the concentration constant, $K_{\rm p}$, of the disproportionation reaction:

In the halide systems two mononuclear complexes CuX and CuX₂⁻ are formed. The solubility products of CuX, pK_{sp} , are 16.0, 15.8 and 17.9 and overall formation constants of CuX₂⁻, $\log \beta_2$ are 19.9, 17.9 and 17.2 for X = Cl⁻, Br⁻ and l⁻, respectively. The results are discussed in terms of solvation of the various complexes.

The hydrated copper(I) ion is unstable in water and in the absence of ligands stabilizing the monovalent state it disproportionates to copper(II) and metallic copper. In some aprotic solvents copper(I) is more solvated than is copper(II) and this causes drastic changes in the relative stabilities of both the oxidation states. The disproportionation constant decreases from ca. 10^6 dm³ mol⁻¹ in water² (W) to ca. unity in dimethyl sulphoxide^{3,4} (DMSO) and becomes very small in pyridine⁵ (PY) (ca. 10^{-14} dm³ mol⁻¹) and in acetonitrile⁶ (AN) (ca. 10^{-21} dm³ mol⁻¹). The strong stabilization of copper(I) in PY and AN facilitates its examination by making the solutions much less sensitive to air oxidation than in DMSO.

Complex formation between metal cation and ligand competes with the solvation of all species involved. As a result, copper(I) forms two soluble CuX and CuX_2^- halide complexes in DMSO,^{3, 4, 7} PY⁵ and AN^{6, 8} in contrast to aqueous solutions in which neutral CuX complexes are only slightly soluble.^{2, 9} In DMSO the CuCl₃⁻ complex is also formed at high ligand concentration.⁴

The formation of copper(II) chloro complexes has been investigated in DMSO,^{3,7,10,11} dimethylformamide,^{12,13} AN,¹³ tetrahydrofuran¹⁴ and propylene carbonate^{11,15} (PC). This paper deals with the investigation of the thermodynamic stability of copper(I) and its halide-complex formation in PC, this solvent having a high dielectric constant and poor solvation ability towards cations.

Experimental

Materials

Propylene carbonate (Merck, 99%) was shaken with solid KMnO₄, filtered and heated at *ca*. 100 °C for 3 h. After having been cooled and filtered it was twice distilled at *ca*. 1 mmHg^{\dagger} through a 50 cm Vigreux column.

Tetraethylammonium perchlorate (Et₄NClO₄) was prepared by mixing equimolar

 $\dagger 1 \text{ mmHg} = 101325/760 \text{ Pa}.$

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aqueous solutions of Et_4NCl (Fluka) and $AgClO_4$. The silver chloride precipitate was filtered off and a small amount of Et_4NCl was dissolved in the filtrate. The solution was shaken with Ag_2O suspension, filtered and evaporated to small volume. The crystals of Et_4NClO_4 obtained on cooling were recrystallized twice from ethanol and dried under vacuum at 70 °C.

Tetraethylammonium chloride and iodide (Fluka) and tetrabutylammonium bromide (Reachim, USSR) were dried at 110 °C in a vacuum oven and were stored over P_2O_5 in a vacuum desiccator before being used as sources of halide anions. Nitrosyl perchlorate was obtained as described by Hathaway and Underhill.¹⁶ Cu(ClO₄)₂ · 4AN was prepared by oxidation of copper powder (Merck) with nitrosyl perchlorate.¹⁷ CuClO₄ · 4AN was prepared by the reduction of an AN solution of copper(II) perchlorate with copper powder. It was recrystallized from AN and dried under vacuum. Cu(ClO₄)₂ · 6H₂O (Merck) was dried *in vacuo* at 40 °C.

Stock solutions of copper(II) in PC were obtained by dissolving $Cu(ClO_4)_2 \cdot 4AN$ or $Cu(ClO_4)_2 \cdot 6H_2O$ in PC and stirring the solutions under vacuum at 40 °C for several hours, in order to reduce the acetonitrile or water content, respectively. $CuClO_4 \cdot 4AN$ was used as the source of copper(I) cations in preparation of PC solutions of $CuClO_4$. These were stable for *ca*. 2–3 days if kept in a closed vessel under an inert gas atmosphere. After this period of time, or after *ca*. 1 h if warmed under vacuum, the solutions became turbid. To minimize the AN content in the Cu^T solutions used in standard electrode potential studies, the solutions were stirred under vacuum at 40 °C for *ca*. 2 h and used immediately after preparation. In complex-formation studies AN was removed as described later.

Apparatus and Experimental Procedures

The value of the formal standard potential of the Cu/Cu^{2+} couple was established by measuring the electromotive forces of the cell (1) at varying Cu^{II} concentrations:

$$Cu(Hg) | Et_{4}NClO_{4} (0.1 \text{ mol } dm^{-3}), Cu^{11}, PC |$$

 Et_4NClO_4 (0.1 mol dm⁻³), PC

 Et_4NClO_4 (0.1 mol dm⁻³), AgClO₄ (0.01 mol dm⁻³), AN | Ag. (1)

For the reference half-cell, readily available anhydrous $AgClO_4$ and twice-distilled AN (Merck) have been used. The silver wire, serving as an electrode, was polished with fine emery paper before each use. In the left half-cell a dropping copper-amalgam electrode was used. The variation of the Cu^{II} concentration in cell (1) was not realized by the usual titration procedure, because the e.m.f. values drifted slowly with time, probably as a result of the reduction of Cu^{II} in contact with the amalgam. Equilibrium e.m.f. values for various Cu^{II} concentrations were measured in separate experiments. The left-hand half-cell compartment was filled with the Cu^{II} solution and connected to the salt bridge and the reference; after *ca*. 5 min the indicating amalgam electrode was immersed in the Cu^{II} solution and the potential was measured as soon as possible (after *ca*. 2 min), and then observed for *ca*. 1 h. The equilibrium e.m.f. values were determined by extrapolation of measured potentials to zero time and finally recorded with an accuracy of ± 1 mV. The corresponding quantity for aqueous solution was determined by direct titration.

Some attempts were made to determine directly the Cu/Cu^+ couple standard potential. In order to measure the Cu(Hg)- or Cu(solid)-electrode potential at various Cu^{I} concentrations, 0.1 mol dm⁻³ Et₄NClO₄ solution was titrated with Cu^I. In both cases the reproductibility of measured e.m.f. was very poor; the response of the electrodes (*E*/decade in concentration) was much lower than expected from the Nernst equation, so that the standard potential could not be estimated directly. To determine



Fig. 1. The electrode potential of the Cu/Cu²⁺ couple in PC as a function of log [Cu²⁺]. Medium : Et_4NClO_4 (0.1 mol dm⁻³); T = 25 °C.

the standard potential of the Cu^+/Cu^{2+} couple, the copper(I) solutions were titrated with the copper(II) in the half-cell (2)

$$Pt | Et_4 NClO_4 (0.1 \text{ mol } dm^{-3}), Cu^1, Cu^{11}, PC |.$$
(2)

Pt foil sealed in a glass tube served as an indicating electrode.

In the complex-formation studies the ligand solution was added from an automatic dispenser (Unipan, type 336B, Poland) to the half-cell (3) compartment containing the copper(I) solution: $Cu(Hg) \downarrow Et NCIO (0.1 mol dm^{-3}) Cu^{I} X^{-} PC$ (3)

$$Cu(Hg) | Et_4 NClO_4 (0.1 \text{ mol } dm^{-3}), Cu^{-1}, X^{-1}, PC.$$
 (3)

In some experiments, in order to avoid the presence of AN molecules introduced into the copper(1) solutions with $CuClO_4 \cdot 4AN$ crystals, the insoluble CuX complexes were precipitated from PC; they were washed on a vacuum glass filter with 0.1 mol dm⁻³ Et₄NClO₄ solution in PC, transferred to the cell (3) compartment containing the supporting electrolyte solution, and titrated against the ligand solution. The copper content was analysed by EDTA titration as described later.

The half-cells (2) and (3) were connected to the same silver reference as used in the cell (1).

In experiments with copper(1) all solutions were deaerated with argon which was also passed over their surfaces during the e.m.f. readings.

The cells were jacketted and the temperature was maintained at 25 °C by means of a water-circulating thermostat. Potentials were measured with a high-impedance digital voltmeter (Meratronik, type V541, Poland) with an accuracy of ± 0.1 mV. The copper content in both the tested and stock solutions was determined by EDTA titration against Murexide as an indicator in aqueous buffered media. The copper(I) ions were oxidized with nitric acid solution before titration.

Results and Discussion

Electrode Potentials and Copper(I) Disproportionation

To determine the formal standard potential (*E*, when the concentration quotient, not the activity quotient, is unity) of the Cu/Cu²⁺ couple, the e.m.f. of cell (1) was plotted against $\log[Cu^{2+}]$ and extrapolated to $\log[Cu^{2+}] = 0$ (fig. 1). The slope is *ca*. 32 mV, a little higher than that expected from the Nernst equation.

The e.m.f. values of cell (2) plotted vs. $\log ([Cu^{2+}]/[Cu^{+}])$ give a straight line with a slope of 60 mV (fig. 2). The e.m.f. at $\log ([Cu^{2+}]/[Cu^{+}]) = 0$ corresponds to the formal standard potential of the Cu⁺/Cu²⁺ couple. The same results have been obtained with

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Fig. 2. Determination of the formal standard potential of the Cu⁺/Cu²⁺ couple in PC. Medium : Et_4NClO_4 (0.1 mol dm⁻³); T = 25 °C.

Table 1. Formal standard potentials (mV) of the Cu/Cu^+ , Cu/Cu^{2+} and Cu^+/Cu^{2+} couples in PC, together with the disproportionation constant $K_D(PC) = [Cu^{2+}]/[Cu^+]^2$ and the Cu/Cu^{2+} couple potential in water^a

	PC	W	
$E_0(Cu/Cu^+)$	130 ± 3		
$E_0(Cu/Cu^{2+})$	231 ± 1	-152 ± 2	
$E_0(Cu^+/Cu^{2+})$	332 ± 2		
$\log K_{\rm D}$	-3.44 ± 0.2		

^a Medium: Et₄NClO₄ (0.1 mol dm⁻³); T = 25 °C; potentials are referenced to Ag/Ag⁺ (0.01 mol dm⁻³), Et₄NClO₄ (0.1 mol dm⁻³), AN. The limits of error refer to standard deviations.

the use of $Cu(ClO_4)_2 \cdot 6H_2O$ and $Cu(ClO_4)_2 \cdot 4AN$ as copper(II) sources. From these values and equations:

$$E_0(Cu/Cu^+) = 2E_0(Cu/Cu^{2+}) - E_0(Cu^+/Cu^{2+})$$
(4)

$$\log K_{\rm D} = [E_0({\rm Cu}/{\rm Cu}^+) - E_0({\rm Cu}^+/{\rm Cu}^{2+})]/59 \text{ mV}$$
(5)

the complete set of electrode potentials can be obtained together with the disproportionation constant value (table 1). The concentration equilibrium constant $K_{\rm D}$, measured in 0.1 mol dm⁻³ Et₄NClO₄ and calculated from eqn (5) can be corrected in order to estimate the thermodynamic equilibrium constant. Neglecting the possibility of ion-pairing, and assuming an activity coefficient of $\gamma_1 = 10^{-0.16}$ for singly charged ions and $\gamma_2 = 10^{-0.49}$ for doubly charged ions,¹⁸ a value of $K_{\rm D} = -3.44 - 0.17 = -3.61$ was obtained. The decrease in the disproportionation constant when the Cu–Cu^I–Cu^{II}

and

system is transferred from water to PC reflects the changes in solvation of both oxidation states, according to the following thermodynamic cycle:



and the equation:

 $2.303RT \log [K_{\rm D}(W)/K_{\rm D}(PC)] = \Delta G_{\rm t}^{\infty}(Cu^{2+}) - 2\Delta G_{\rm t}^{\infty}(Cu^{+})$ (7)

where $\Delta G_t^{\infty}(\operatorname{Cu}^{n+})$ is the free energy of Cu^{n+} transfer from water to PC. The superscript ∞ denotes the hypothetical ideal 1 mol dm⁻³ Cu^I or Cu^{II} solution in both solvents. While the disproportionation constant values are accessible on the basis of rigorous thermodynamics, the determination of the transfer free-energies of individual ions, which appear in eqn (6) and (7), can be carried out only by the use of extra-thermodynamic assumptions. From the Cu/Cu²⁺ couple formal standard potentials in PC and water, listed in table 1, the value of $\Delta G_t^{\infty}(\operatorname{Cu}^{2+}, W \to PC) = 73.9 \text{ kJ mol}^{-1}$ was estimated, assuming that the liquid junction potential between the solutions in both solvents is negligible:

$$\Delta G_{\rm t}^{\infty}({\rm Cu}^{2+},{\rm W}\to{\rm PC}) = 2F[E_0({\rm Cu}/{\rm Cu}^{2+},{\rm PC}) - E_0({\rm Cu}/{\rm Cu}^{2+},{\rm W})]$$
(8)

 $\Delta G_t^{\infty}(\mathrm{Cu}^+, \mathrm{W} \to \mathrm{PC}) = 10.0 \text{ kJ mol}^{-1}$ was calculated from eqn (7) assuming that $\log K_{\mathrm{D}}(\mathrm{W}) = 6$. For these calculations no corrections were made for Debye–Hückel effects, because these corrections are commonly of the order of 1 kJ mol}^{-1} for solutions having high dielectric constants, and are largely cancelled when ΔG_t^{∞} values are calculated.¹⁹

The transfer free-energies estimated here from the formal standard potentials agree well with the literature data. $\Delta G_t^{\infty}(Cu^{2+}, W \rightarrow PC) = 18.2 \text{ kcal mol}^{-1} (76.2 \text{ kJ mol}^{-1})$ can be calculated from $\Delta G_t^{\infty}(Cu^{2+}, W \rightarrow AN)$ and $\Delta G_t^{\infty}(Cu^{2+}, AN \rightarrow PC)$ obtained by Cox *et al.*²⁰ from the potential of Pt/Cu⁺ (0.01 mol dm⁻³), Cu²⁺ (0.01 mol dm⁻³), PC couple and by extrapolation of measured potentials of the Cu/Cu⁺ (0.01 mol dm⁻³), AN+PC couple to [AN] = 0. Coetzee and Istone²¹ report 17.9 kcal mol⁻¹ (74.9 kJ mol⁻¹) for the $\Delta G_t^{\infty}(Cu^{2+}, W \rightarrow PC)$ determined with the use of a copper ion-selective electrode. $\Delta G_t^{\infty}(Cu^+, W \rightarrow PC) = 2.5 \text{ kcal mol}^{-1}$ (10.5 kJ mol⁻¹) can be calculated from the data reported by Cox *et al.*¹⁸

The estimated transfer free-energies indicate weaker solvation of both the copper oxidation states in PC than in water. However, PC is the weakest copper(II) solvator in the order of solvents for which $\Delta G_t^{\infty}(Cu^{2+})$ has been studied.^{1, 20-23} Therefore, copper(I) is much more stable in PC than in aqueous solution mainly because of very poor copper(II) solvation and not to an increase in copper(I) solvation.

Complex Formation

The shape of the curves obtained from cell (3) when copper(1) was titrated with the halide solution, is shown in fig. 3. There are two inflection points at halide: copper ratios of 1:1 and of 2:1, indicating the stoichiometry of the complexes formed. Two well defined plateaus can also be seen, the first between both inflection points, and the second at higher ligand concentrations. Up to a halide: copper(1) ratio of ca. 2, the solutions are





Fig. 3. Titration of 5.4 cm^3 Cu⁺ (0.0044 mol dm⁻³) with Br⁻ (0.025 mol dm⁻³). Medium: Et₄NClO₄ (0.1 mol dm⁻³); T = 25 °C.



Fig. 4. Determination of the $\log \beta_2$ values. 4.4 cm³ Cu⁺ (0.00545 mol dm⁻³), 5.4 cm³ Cu⁺ (0.0044 mol dm⁻³) and 4.0 cm³ Cu⁺ (0.00185 mol dm⁻³) were titrated with (a) Cl⁻ (0.0218 mol dm⁻³); (b) Br⁻ (0.025 mol dm⁻³); (c) I⁻ (0.01 mol dm⁻³), respectively. 2.8 < $[X^-]_0 / [Cu^+]_0 < 17.5$; medium: Et₄NClO₄ (0.1 mol dm⁻³); T = 25 °C.

in equilibrium with the CuX(solid) precipitated after the addition of the first drops of the halide solution to copper(I).

The following equilibria have been assumed to hold for all solutions formed during titration: β_{i}

$$Cu^{+} + X^{-} \stackrel{p_{1}}{\underset{a}{\longrightarrow}} CuX \tag{9}$$

$$Cu^{+} + 2X^{-} \rightleftharpoons^{\mu_{2}} CuX_{2}^{-}$$
(10)



Fig. 5. Determination of the solubility product values. $4.4 \text{ cm}^3 \text{ Cu}^+$ (0.00545 mol dm⁻³), 5.4 cm³ Cu⁺ (0.0044 mol dm⁻³) and 4.0 cm³ Cu⁺ (0.00185 mol dm⁻³) were titrated with (a) Cl⁻ (0.0218 mol dm⁻³); (b) Br⁻ (0.025 mol dm⁻³); (c) I⁻ (0.01 mol dm⁻³), respectively. $1 < [X^-]_0/[\text{Cu}^+]_0 < 2$; medium: Et₄NClO₄ (0.1 mol dm⁻³); T = 25 °C.

and the additional equilibrium which holds only in solutions saturated with the solid precipitated: K_{sn}

$$\operatorname{CuX}(\operatorname{solid}) \stackrel{\kappa_{\operatorname{sp}}}{\rightleftharpoons} \operatorname{Cu}^{+} + X^{-}.$$
(11)

The overall formation constant β_2 for CuX_2^- can be calculated from the upper plateau, taking into account mass-balance equations for total ligand, $[X^-]_0$, and copper(I), $[Cu^+]_0$, concentrations:

$$[X^{-}]_{0} = [X^{-}] + \beta_{1}[Cu^{+}][X^{-}] + 2\beta_{2}[Cu^{+}][X^{-}]^{2}$$
(12)

$$[Cu^{+}]_{0} = [Cu^{+}] + \beta_{1}[Cu^{+}][X^{-}] + \beta_{2}[Cu^{+}][X^{-}]^{2}.$$
(13)

Using the Nernst equation for the free copper(I) concentration, an expression for the e.m.f. values of cell (3) can be obtained:

$$E = E_0(Cu/Cu^+) - b \log \beta_2 + b \log ([CuX_2^-]/[X^-])$$
(14)

where b = 2.303 RT/F. Assuming that at large ligand:copper ratios the concentrations of CuX are negligible and that practically the whole amount of Cu⁺ is complexed, the following equation can be written:

$$E = a + b \log \{ [Cu^+]_0 / ([X^-]_0 - 2[Cu^+]_0)^2 \}.$$
 (15)

The experimental data were analysed with the help of this method (fig. 4) and in all cases the factor b which appears in eqn (15) was found to be close to 59 mV, which suggests that the Cu(Hg)/Cu⁺ indicating electrode works properly in the solutions containing ligands. The concentration of the CuX_2^- complex (ignoring CuX) is given

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Table 2. The overall stability constants β_1 and solubility products pK_{sp} (calculated as concentration quotients) for CuX and CuX₂⁻ complexes formed in PC, together with the literature data for other solvents. T = 25 °C.

	Cl-	Br−	I-	ref.
	PC (med	ium : Et, NCl	O, 0.1 mol di	m ^{−3})
$pK_{sn}(CuX)$	16.0 ± 0.2^{a}	15.8 ± 0.1	17.0 ± 0.1	this
$\log \beta_{0}(CuX_{0}^{-})$	19.9 ± 0.2	17.9 ± 0.1	17.2 ± 0.1	work
	water (n	nedium: NaC	ClO_{4} 5 mol dr	n ⁻³)
$pK_{sn}(CuX)$	7.38	8.89	12.72	9
$\log \beta_{0}(CuX_{2})$	6.0	6.28	8.6	
0, 2, 2,	AN (med	lium : Et ₄ NC	IO, 0.1 mol d	m ⁻³)
$\log \beta_1(CuX)$	4.3	3.5	*3.1	8
$\log \beta_{2}(CuX_{2})$	10.2	7.3	5.8	
	AN (med	lium : Et ₄ NC	IO, 0.1 mol d	m ⁻³)
$\log \beta_1(CuX)$	4.02	3.39 *	3.13	6
$\log \beta_{2}(CuX_{2})$	9.55	7.21	5.21	
0,2(2)	DMSO (m	edium: NH	ClO ₄ 0.1 mol	dm-3)
$\log \beta_1(CuX)$	4.37	4.19	4.83	4
$\log \beta_{2}(CuX_{2}^{-})$	8.87	7.94	7.64	
0, 2, 2,	DMSO (m	edium: Et₄N	ClO ₄ 0.1 mol	dm ⁻³)
$\log \beta_1(CuX)$	6.0	5.0	5.5	3
$\log \beta_{0}(CuX_{2}^{-})$	11.95	9.6	8.2	
0.1	PY (med	ium: Et₄NCl	$O_4 0.1 \text{ mol dr}$	n⁻³)
$\log \beta_1(CuX)$	3.09	2.78	2.69	5
$\log \beta_{s}(CuX_{s})$	5.00	3.88	3.59	
2, 2, 2,				

^a The limits of error refer to standard deviations.

by $[CuX_2^-] = [Cu^+]_0/(1 + \beta_2^{-1}[X^-]^{-2})$. Concentrations used for these studies were $1 < [Cu^+]_0/10^{-3}$ mol dm⁻³ < 7 and $[X^-] > 2.8[Cu^+]_0$. Since the lowest β_2 value is of the order of 10^{17} , then $(\beta_2[X^-]^2)^{-1}$ is of the order of 10^{-11} , so that

$$[CuX_2^-] = [Cu^+]_0 / (1 + 10^{-11})$$

and no concentration corrections are necessary in β_2 calculations.

In the region of the titration curve where solid CuX is present, the mass balances (12) and (13) include an additional term for the amount of the precipitated solid. This term can be eliminated by subtraction of eqn (13) from (12):

$$[X^{-}]_{0} - [Cu^{+}]_{0} = [X^{-}] - [Cu^{+}] + \beta_{2}[Cu^{+}][X^{-}]^{2}.$$
 (16)

Substitution of the solubility product expression into (16) gives

$$([X^{-}]_{0} - [Cu^{+}]_{0} + [Cu^{+}])[Cu^{+}] = K_{sp} + K_{sp}^{2}\beta_{2} = \text{const.}$$
(17)

Therefore the electromotive force of cell (3) in this region of the titration curve is given by $F = a' - h \log(|X^-| - |Cu^+|)$ (18)

$$E = a' - b \log ([X^{-}]_{0} - [Cu^{+}]_{0}).$$
(18)

Eqn (18) has been obtained taking into account that $[Cu^+] \ll [X^-]_0 - [Cu^+]_0$.

As the equilibrium constants β_2 are known from the analysis of the upper plateau, and quantities on the left side of eqn (17) are directly measurable, the solubility product values can be obtained from the titration points along the lower plateau. The e.m.f. values plotted against log $([X^-]_0 - [Cu^+]_0)$ give straight lines of slope in the range 60–62 mV (fig. 5), which serves as a check for the indicating electrode in this region. On the other hand, there is a systematic deviation of the values calculated from the data

measured near the inflection points, probably arising from the system's failure to reach equilibrium. Determined K_{sp} and β_2 values are collected in table 2, together with the literature data for other solvents. Activity-coefficient corrections for β_2 and K_{sp} give the relationship $\log \beta_2$ (or K_{sp}) = $\log \beta_2$ (or K_{sp}) + 0.32.

The most striking feature of neutral CuX complexes in PC, as compared with those formed in AN, DMSO and PY, is their solid-precipitate formation. The concentration of undissociated CuX is constant in all solutions saturated with the CuX(solid):

$$[CuX] = \beta_1 K_{sp} = const.$$
(19)

The solubility S of the CuX(solid) is determined by the concentrations of both free and complexed copper(I): G = V = (I + I) + 0(20)

$$S = K_{\rm sp}([X^{-}]^{-1} + \beta_1 + \beta_2[X^{-}]).$$
⁽²⁰⁾

In the PC-AgCl system, for which both $\beta_1(AgCl)$ and $K_{sp}(AgCl)$ values are known, the solubility of pure AgCl in pure PC is determined mainly by the concentration of the undissociated AgCl complex.¹⁸ The $\beta_1(CuX)$ values are unknown at the moment, but if the predominating soluble species in solutions saturated with the CuX(solid) are CuX and CuX₂⁻ complexes (the latter in the CuX/X⁻/PC system), the square root of the solubility product of the CuX(solid) is not equal to its solubility, by analogy to the AgCl-PC system.

In the protic solvent water, the chloride ion is much more solvated than bromide and iodide ions, because of the ability of water molecules to form stronger hydrogen bonds with chloride. Consequently, the stabilities of the CuX_2^- complexes follows the order $Cl^- < Br^- < I^-$. In PC, as well as in other aprotic solvents, where hydrogen bonds cannot be formed, this sequence is reversed, which reflects the sequence of $\Delta G_t^{\infty}(X^-, W \rightarrow PC)$ values. Marcus²³ reviewed $\Delta G_t^{\infty}(X^-, W \rightarrow PC)$ obtained by a number of authors using a variety of procedures. The selected values are 39.8, 30.0 and 13.7 kJ mol⁻¹ for Cl⁻, Br⁻ and I⁻, respectively. Owing to the poor solvating ability of PC molecules towards both copper(1) and halide ions, much more stable complexes are formed in PC than in other solvents.

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