Halogenocomplexes of copper(II) in anhydrous propan-2-ol.

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HALOGENOCOMPLEXES OF COPPER(II) IN ANHYDROUS PROPAN-2-OL

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Abstract—Solutions of copper(II) halides in propan-2-ol were investigated spectrophotometrically at 25°C and at constant ionic strength. For the chlorides as well as the bromides four mononuclear complexes are present in the solutions and their overall stability constants were calculated as $\log \beta_{CuCl^+} = 5.7$, $\log \beta_{CuCl_2} = 8.6$, $\log \beta_{CuCl_3^-} = 10.2$, $\log \beta_{CuCl_4^{2-}} = 10.6$, and $\log \beta_{CuBr^+} = 6.1$, $\log \beta_{CuBr_2} = 8.4$, $\log \beta_{CuBr_3^-} = 10.2$, $\log \beta_{CuBr_4^{2-}} = 10.7$. Electronic spectra of all the species present in the solution were calculated; the tetrahalogenocuprate CuX_4^{2-} has D_{2d} symmetry.

A comparative study of the thermodynamic stabilities of these complexes in alcohols shows a tendency of stability as an increasing function of number of carbon atoms in the alcohol.

In this paper we present the results of a spectrophotometric study of the copper(II) halide complexes in propan-2-ol with a view to determine the solvent effects on the thermodynamic and spectroscopic properties of these complexes in alcohols. An exhaustive bibliography of copper(II) halogenocomplexes in aqueous as well as in organic solutions has already been reported in our earlier publications,[1,2] we shall therefore limit our bibliographic references to studies carried out in alcoholic medium only.

There are hardly any quantitative studies in alcohols reported in the literature. In one of the earlier works, Kosower *et al.*[3] who observed six absorption bands propose the existence of six bromocomplexes in ethanol. Barnes and Hume[4] have identified the

absorption maximum at 625 nm in ethanol as that of the tribromocuprate. Furlani and co-workers have discussed the configurations of the tetrahalogenocuprates as D_{2d} or D_{4h} in different organic solvents.[5,6]

Our results of the studies of these complexes in methanol[1] and ethanol[2] have shown the presence of four mononuclear complexes in both the alcohols. Overall stability constants as well as individual electronic spectra of all species were calculated and the structures in solution of the tetracoordinated complexes were discussed. We now report the results of the copper(II) halide complexes in propan-2-ol. The successive equilibria, the simplified representation of which does not take into account the solvated character of the copper(II) in the inner coordination sphere, $Cu^{2+} + jX^- \rightleftharpoons CuX_j^{(j-2)-}$ ($X = Cl$, Br), were studied at 25°C and at constant ionic strength maintained at 1 mol dm^{-3}. Overall

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stability constants, β_j, for the species present were calculated using experimental data of absorption measurements in the UV, vis and the near-IR regions and these parameters in turn were used to calculate the individual electronic spectrum of the species. We do emphasize that β_j are apparent stability constants, calculated in the approximation of no occurrence of ion-pairing of the different species present in the non-aqueous medium.

EXPERIMENTAL

Anhydrous propan-2-ol. Merck p.a., was used. Stock solutions were prepared from $Cu(ClO_4)_2 \cdot 6H_2O$, $LiClO_4$, LiCl, (Fluka) and LiBr (Merck p.a.). Copper solution was titrated against EDTA using murexide as an indicator.[7] Ionic strength was kept constant at 1 mol dm^{-3} with the help of lithium perchlorate. Ligand concentrations were kept higher in order to eliminate the possibilities of formation of plurinuclear complexes on the one hand and favour the formation of highly coordinated complexes such as CuX_4^{2-} on the other hand.

Since copper(II) halide solutions are not very stable, especially the bromide solutions, all measurements were made immediately after the addition of the last reactant. The experimental conditions, in short, were identical to those in studies in methanol and ethanol in order to make a uniform comparison.

RESULTS AND DISCUSSION

Experimental spectra

Figures 1 and 2 represent the experimental spectra of copper(II) chlorides and bromides, respectively.

In the case of chloride solutions the free solvated copper ion seems to have its absorption maximum at ca 240 nm. As soon as small quantities of ligand are added an absorption band at 270 nm appears and progressively shifts to 290 nm for $C \geqslant 0.004$ mol dm^{-3}. For ligand concentrations higher than 0.008 mol dm^{-3} a shoulder peak is noticed at ca 250 nm, and for still higher concentrations a large band centred at 390 nm is observed along with isobestic points at 264, 308 and 366 nm. In the near-IR region, Cu^{2+} has its characteristic absorption at 800 nm which, as the ligand is added, shifts regularly until 960 nm. For solutions of higher concentrations a large band appears at about 1100 nm.

In the bromide solutions, even at very dilute ligand concentrations, a maximum is observed at 310 nm which for $C > 0.02$ mol dm^{-3} splits in two:
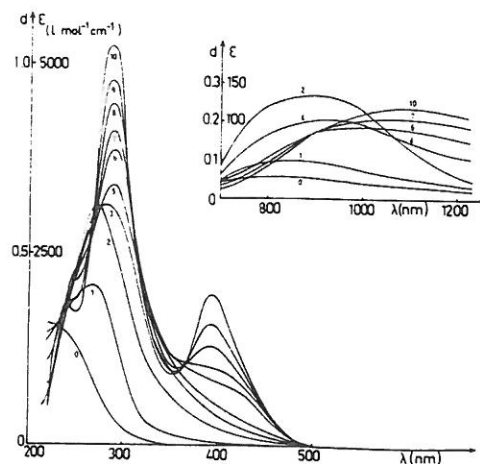

Fig. 1. Absorption spectra of copper(II) in lithium chloride–perchlorate isopropanolic mixtures. $B = 1 \times 10^{-3}$ M. $l = 0.2$ cm (UV–vis). 2 cm (near-IR). Spectra/$[Cl^-]_0$: 0/0; 1/0.001; 2/0.002; 3/0.004; 4/0.008; 5/0.01; 6/0.04; 7/0.08; 8/0.20; 9/0.40; 10/1.0.

one at 280 and the other at 350 nm. The absorption band at 280 nm undergoes a hypsochromic shift to 270 nm. In the vis spectrum there are two large bands at 510 and 640 nm. Finally in the IR region, the absorption maximum of the copper ion at 800 nm is progressively shifted with the addition of bromide ions from 860 to 940 nm in a quite similar way to the chloride system. For $C > 0.08$ mol dm^{-3} this maximum shifts from 940 to 1100 nm, which is probably due to the change in configuration of the tetracoordinated complex.

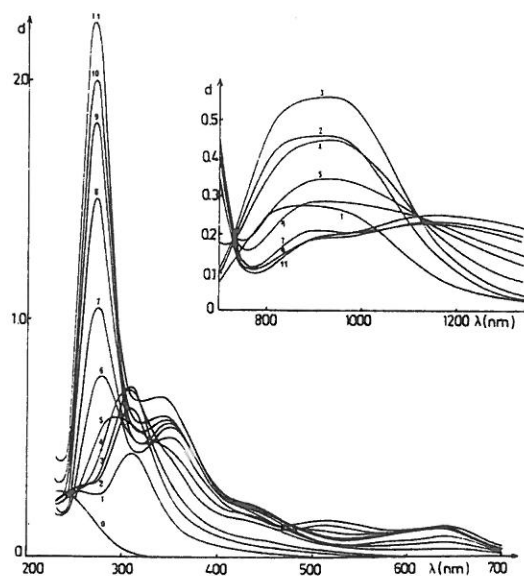Fig. 2. Absorption spectra of copper(II) in lithium bromide–perchlorate isopropanolic mixtures. $B = 1 \times 10^{-3}$ M; $l = 0.2$ cm (UV–vis). 2 cm (near-IR). Spectra/$[Br^-]_0$: 0/0; 1/0.001; 2/0.002; 3/0.003; 4/0.010; 5/0.02; 6/0.04; 7/0.10; 8/0.20; 9/0.40; 10/0.80; 11/1.0.

Numerical analysis and stability constants

A matrix rank treatment, based on the method of Hugus and El Awady was used to determine the minimum number of absorbing species in the solution.[8] These calculations were carried out on an experimental data set of $N \times L = 400$ absorption measurements for the chlorides (number of wavelength $L = 16$, number of solutions $N = 25$) and 392 measurements ($N = 14$, $L = 28$) for the bromides. The details of the mathematical expressions used for calculations have already been given in our earlier publications.[9,10]

For both the systems, results indicate the presence of at least three complexes. Taking into account these results and the fact that experimental conditions are such that the formation of plurinuclear complexes is negligible, theoretical models for three and four mononuclear complexes, i.e. CuX^+, CuX_2, CuX_3^- and CuX^+, CuX_2, CuX_3^- and CuX_4^{2-}, respectively, were tested and their results summarized in Table 1.

Several initial assumptions are used for the thermodynamic basis of the stability constant of a complex in this kind of non-aqueous solutions:

(1) A stabilization of the ionic environment of the metal is obtained by addition of concentrated electrolytes which do not interfere in the coordination process between metal and ligand. The activity coefficients of the different reacting species will be stabilized in constant ionic strength medium as they are in aqueous solutions. Their values will certainly differ from one non-aqueous medium to

another, but it is demonstrated that the ratio of the activity coefficients of the species inherent in superposed equilibria will be constant.

(2) Protic solvents such as propan-2-ol are classified as weakly dissociating solvents having a good ionizing ability according to the dielectric constant values of the pure solvents lying over 20: introducing strong electrolyte mixtures within the medium will certainly, despite constant ionic strength, modify the value of this parameter and consequently the dissociating property of the solvent; but the impact of this variation should be negligible for the solvation energies of the free ions as for the complexes. In such a medium the complexes will be present as ions which is not the case in molecular solvents (acetic acid[11] or tetrahydrofuran[12]) where all the species are ion-pairs or ion-aggregates. The assumption is made that in protic solvents such as propan-2-ol the formation of ion-pairs is not taken into account in the numerical analysis and the calculation of the constants β_j. This condition could only be considered if the association constants and activity coefficients of all species involved in the superposed equilibria are known: but these quantities are impossible to measure simultaneously.

(3) Transferring the ionic strength concept to this non-aqueous medium with the assumption of the activity coefficients stabilization, the interpretation of the superposed equilibria in non-aqueous solutions is possible: it leads to "apparent stability constants" which can be used as "thermodynamic parameters". The zero of the thermodynamic constants of complexation could be obtained through equilibria investigations at different constant ionic strengths and extrapolation to zero ionic strength of the obtained apparent stability constants.

It is seen that in both cases the standard deviation for all measurements in the whole spectrum region, σ_t, is better for models with four than the models with three complexes. Adding to this the fact that

Table 1. Overall stability constants, β_j, for copper(II) chloro- and bromocomplexes for [1, 2, 3] and [1, 2, 3, 4] models

Complexes	β_j	[1, 2, 3]	[1, 2, 3, 4]
$CuCl^+$	β_1	1.6×10^5	1.8×10^5
$CuCl_2$	β_2	2.3×10^8	4.1×10^8
$CuCl_3^-$	β_3	4.2×10^9	1.4×10^{10}
$CuCl_4^{2-}$	β_4	—	3.7×10^{10}
σ_{UV-vis}		0.071	0.031
σ_{IR}		0.147	0.119
σ_t		0.118	0.089
$CuBr^+$	β_1	8.8×10^2	1.3×10^6
$CuBr_2$	β_2	3.5×10^4	2.6×10^8
$CuBr_3^-$	β_3	4.1×10^5	1.6×10^{10}
$CuBr_4^{2-}$	β_4	—	5.1×10^{10}
σ_{UV-vis}		0.114	0.067
σ_{IR}		0.088	0.088
σ_t		0.104	0.076

Table 2. Coordinates of experimental and calculated isobestic points for [1, 2, 3] and [1, 2, 3, 4] models: λ_{iso} [nm] (ε_{iso} [dm^3 mol^{-1} cm^{-1}])

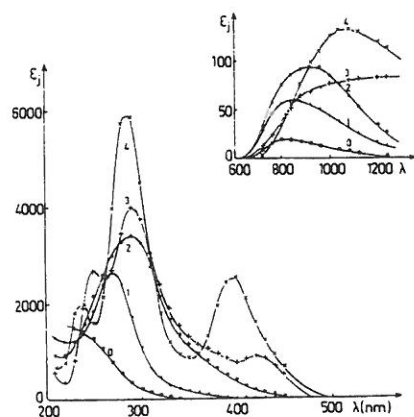|		Calculated	
	Experimental	[1, 2, 3]	[1, 2, 3, 4]
Chlorides	264 (2600)	266 (2860)	263 (2560)
	308 (3250)	310 (2800)	307 (3320)
	365 (1050)	362 (980)	365 (1080)
Bromides	486 (675)	500 (640)	485 (680)
	590 (580)	595 (575)	590 (580)

Fig. 3. Calculated electronic spectra of copper(II) chlorocomplexes in anhydrous isopropanol solutions: Cu('PrOH)$_4^{2+}$ [0]; CuCl$^+$ [1]; CuCl$_2$ [2]; CuCl$_3^-$ [3]; CuCl$_4^{2-}$ [4].

the calculated and experimental isobestic points are in harmony in the case of four complexes (Table 2), we postulate the presence of CuX$^+$, CuX$_2$, CuX$_3^-$ and CuX$_4^{2-}$ in propan-2-ol.

With the help of the overall stability constants already determined, we calculated the individual electronic spectra of all species present in the solution. This is represented in Figs 3 and 4 and the principal absorption bands are summarized in Table 3.

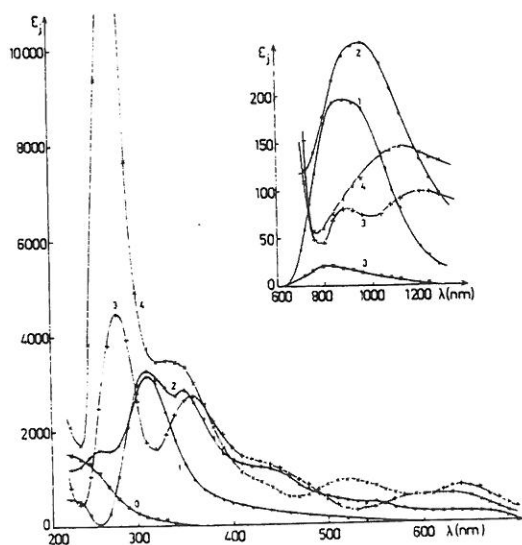Both the tetracoordinated complexes have their d–d transitions at about 1100 nm, a position which

Fig. 4. Calculated electronic spectra of copper(II) bromocomplexes in anhydrous isopropanol solutions: [Cu('PrOH)$_4^{2-}$ [0]; CuBr$^+$ [1]; CuBr$_2$ [2]; CuBr$_3^-$ [3]; CuBr$_4^{2-}$ [4].

Table 3. Principal absorption bands of all species present in propan-2-ol

	Chlorocomplexes	Bromocomplexes
	λ_{max} [nm] (ε_{max} [dm^3 mol^{-1} cm^{-1}])	
Cu^{2+}	<225 (1800)	<225 (1800)
	800 (22)	800 (22)
CuX$^+$	270 (2650)	310 (3180)
	840 (60)	870 (195)
CuX$_2$	290 (3440)	260 (1600)
		310 (3300)
		440 (1200)
	920 (95)	960 (256)
CuX$_3^-$	250 (2680)	280 (4450)
	292 (4000)	360 (2750)
	420 (940)	440 sh
		640 (800)
		880 (80)
	1120 (82)	1200 (98)
CuX$_4^{2-}$	240 (2000)	270 (13440)
	285 (5000)	340 (3450)
	396 (2550)	520 (920)
		620 sh
	1080 (135)	1120 (140)

is commonly admitted to be due to a flattened tetrahedron and assigned to D_{2d} symmetry.[13,14]

The distribution curves of the copper(II) complexes are very similar in the chloride and bromide systems: the degree of formation of the chlorocomplexes confirms the superposition of equilibria for both systems: whatever the ligand concentration there is a simultaneous presence of at least two complexes.

For a comprehensive comparison in alcohols of stabilities and electronic spectra more than three

Table 4. Log β_j of the copper(II) halogeno-complexes in the three alcohols

	Solvent		
Complexes	Methanol	Ethanol	Isopropanol
CuCl$^+$	2.5	3.3	5.7
CuCl$_2$	4.2	6.0	8.6
CuCl$_3^-$	5.4	7.8	10.2
CuCl$_4^{2-}$	5.7	8.3	10.6
CuBr$^-$	3.7	5.0	6.1
CuBr$_2$	5.6	7.8	8.4
CuBr$_3^-$	6.3	9.2	10.2
CuBr$_4^{2-}$	6.3	10.3	10.7

solvents are necessary, therefore a similar study in butanol is desirable and has already been undertaken in our laboratory. This may permit us to establish a few empirical laws in R-OH type solvents. Nevertheless, a tentative comparison of thermodynamic stabilities in the three alcohols, *viz* methanol, ethanol and propan-2-ol is given in Table 4.

A study of the relative stabilities of the chlorides and bromides in the three alcohols brings into prominence two major aspects: (1) in a given solvent the bromides are generally more stable than the chlorides; and (2) the stability of any specific complex increases from methanol to propanol, i.e. the stability of these complexes is directly proportional to the number of carbon atoms in the alcohol.

If this empirical rule is confirmed by the results of our study of these complexes in butanol it can be presumed that an approximate value of the stability constants of the copper(II) halogenocomplexes in the R-OH type solvents can be predicted theoretically.

REFERENCES

1. M. A. Khan, J. Meullemeestre, M. J. Schwing and F. Vierling, *Inorg. Chem.* 1989, **28**, 3306.
2. S. Chafaa, T. Douadi, M. A. Khan, J. Meullemeestre, M. J. Schwing and F. Vierling, *New J. Chem.* 1991, **15**, 39.
3. E. M. Kosower, R. L. Martin and V. M. Meloche, *J. Am. Chem. Soc.* 1957, **79**, 1509.
4. J. C. Barnes and D. N. Hume, *Inorg. Chem.* 1963, **2**, 444.
5. C. Furlani and G. Morpurgo, *Theor. Chim. Acta* 1963, **1**, 102.
6. L. Sestili, C. Furlani, A. Ciani and F. Garbassi, *Electrochem. Acta* 1970, **15**, 225.
7. H. A. Flaschka, *EDTA Titrations*, p. 82. Pergamon Press, Oxford (1964).
8. Z. Z. Hugus and A. A. El Awady, *J. Phys. Chem.* 1971, **75**, 2957.
9. M. Elleb, J. Meullemeestre, M. J. Schwing and F. Vierling, *Inorg. Chem.* 1980, **19**, 2699.
10. F. Vierling, M. J. Schwing and J. Meullemeestre, *Spectra 2000* 1982, **79**, 10.
11. M. A. Khan, J. Meullemeestre, M. J. Schwing and F. Vierling, *Polyhedron* 1990, **9**, 2613.
12. C. Amuli, J. Meullemeestre, M. J. Schwing and F. Vierling, *Inorg. Chem.* 1983, **22**, 3567.
13. B. Morosin and E. C. Lingafelter, *Acta Cryst.* 1960, **13**, 807.
14. B. Morosin and E. C. Lingafelter, *J. Phys. Chem.* 1961, **65**, 50.