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STABILITY AND ELECTRONIC SPECTRA OF COPPER(II) HALIDES IN BUTAN-1-OL AND THE EFFECTS OF R—OH TYPE SOLVENTS ON THESE PROPERTIES

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Abstract—Copper(II) halide complexes were studied in butan-1-ol at 25°C and at constant ionic strength. Formation constants and electronic spectra of all the complexes present in the solution were calculated. The apparent stability of these complexes increases with the number of carbon atoms in the alcohol: the logarithm of the overall stability constant, β_j, is a linear function of their molecular weights. A regular decrease of the stability with the permittivity of the pure solvents is observed. This result is correlated with the increasing dissociating power of the solvents which promotes better hydrogen bonding and hinders the substitution of the solvent molecule by the ligand in the inner coordination sphere of the metal. There is hardly any R—OH-type solvent effect on the electronic spectra of the individual species. Tetrabromocuprate is always present in D_{2d} symmetry, whereas the configuration of tetrachlorocuprate is D_{4h} in methanol and D_{2d} in the higher alcohols.

We have already reported the results of studies of copper(II) halide complexes in methanol,[1] ethanol[2] and propan-2-ol.[3] This paper deals with the results of copper(II) halide complexes in butan-1-ol and the correlation of their properties such as stability, electronic spectra and structure in the alcohols.

$$Cu^{2+} + jX^- \rightleftharpoons CuX_j^{(j-2)-} \quad (X = Cl, Br)$$

The successive equilibria were studied in butanol at 25°C and at constant ionic strength and the overall stability constants, β_j, of the complexes present in solution were calculated. A detailed bibliography on the subject has already been given in our earlier publications.[1,2] We further recall that 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".[3]

EXPERIMENTAL

Butan-1-ol, Prolabo p.a., was used as a solvent. Stock solutions of lithium perchlorate, copper(II) perchlorate, lithium chloride and lithium bromide (all Fluka p.a.) were prepared by dissolving calculated quantities in the solvent. Exact concentrations were determined gravimetrically, except the copper solution which was titrated against EDTA using murexide as an indicator.[4]

Ligand concentrations were kept higher than that of the metal and the ionic strength was kept constant at 1 mol dm^{-3}, as in our earlier work. Experimental conditions were identical to those maintained in other alcohols.

RESULTS AND DISCUSSION

The experimental spectra of the copper(II) chlorides and bromides are represented in Figs 1 and 2, respectively. For the chloride solutions there is an intense absorption at 285 nm in the UV, another large band in the visible at 395 nm and in the IR

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region a maximum at 1050 nm for the analytical ligand concentration $C = 1$ mol dm^{-3}. The presence of four isosbestic points is to be observed at 270, 310, 360 and 920 nm.

The absorption variations of the bromide solutions are, as usual, more complicated than the chlorides. In short, there is an absorption maximum at 305 nm which, at higher ligand concentrations, splits into two bands at 280 and 340 nm. There is another absorption at 580 nm which also splits into a maximum at 525, along with a residual absorption at about 620 nm. Finally, in the IR region, at higher ligand concentrations, there are two absorption maxima at 950 and 1110 nm. In this system there are five isosbestic points, viz. 295, 320, 400, 472 and 1040 nm.

For a numerical analysis, the first step in these types of problems is to determine the number of absorbing species present in the solution. This was determined by the matrix rank treatment method of Hugus and El Awady[5] on a set of experimental data of $N \times L$ absorptions, where L = the number of wavelengths and N = the number of solutions. In all 819 experimental values in the chloride system and 1101 in the bromide system, i.e. 1920 measurements, were computed. The mathematical expressions used in calculations have been explained in our earlier publications.[6,7] As was the case with the first three alcohols, a minimum of three complexes were indicated for the chlorides as well as the bromides. We therefore tested theoretical models [1, 2, 3] and [1, 2, 3, 4], that is for three and four successive mononuclear complexes.

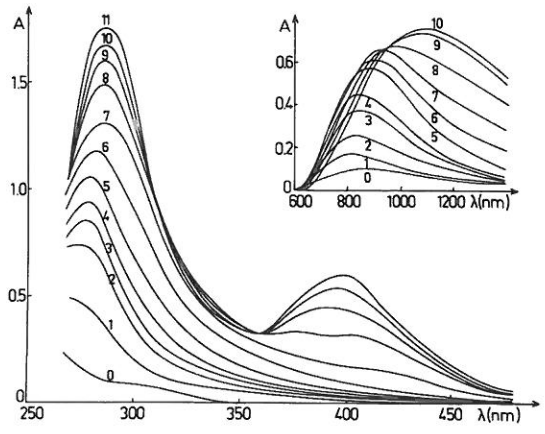


Fig. 1. Absorption spectra of copper(II)–Li$^+$ (Cl^-, ClO_4^-) 1 M solutions in anhydrous butan-1-ol. UV–vis: $[Cu^{II}] = 3 \times 10^{-4}$ mol dm^{-3}; $l_{cuve} = 1$ cm spectrum/$[Cl^-]$ (mol dm^{-3}): 0/0, 1/0.0005, 2/0.001, 3/0.002, 4/0.004, 5/0.008, 6/0.02, 7/0.06, 8/0.2, 9/0.4, 10/0.6, 11/1.0. Near-IR: $[Cu^{II}] = 3 \times 10^{-3}$ mol dm^{-3}; $l_{cuve} = 2$ cm spectrum/$[Cl^-]$ (mol dm^{-3}): 0/0, 1/0.0005, 2/0.002, 3/0.004, 4/0.006, 5/0.02, 6/0.04, 7/0.08, 8/0.2, 9/0.6, 10/1.0.

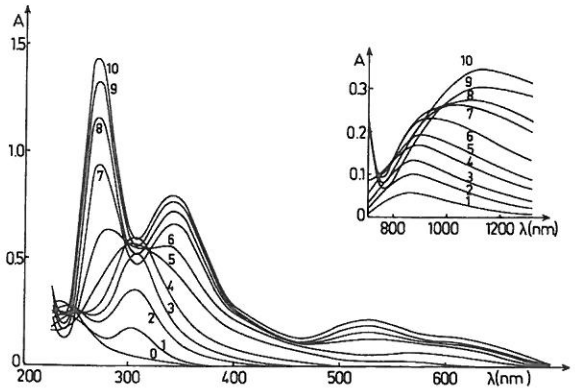


Fig. 2. Absorption spectra of copper(II)–Li$^+$ (Br^-, ClO_4^-) 1 M solutions in anhydrous butan-1-ol. UV–vis: $[Cu^{II}] = 1 \times 10^{-3}$ mol dm^{-3}; $l_{cuve} = 0.2$ cm spectrum/$[Br^-]$ (mol dm^{-3}): 0/0, 1/0.001, 2/0.002, 3/0.004, 4/0.01, 5/0.04, 6/0.1, 7/0.4, 8/0.6, 9/0.8, 10/1.0. Near-IR: $[Cu^{II}] = 1 \times 10^{-3}$ mol dm^{-3}; $l_{cuve} = 2$ cm spectrum/$[Br^-]$ (mol dm^{-3}): 1/0.001, 2/0.003, 3/0.006, 4/0.01, 5/0.02, 6/0.04, 7/0.1, 8/0.4, 9/0.6, 10/1.0.

The results in Table 1 show that whatever the system, the total standard deviation, σ_t, is lower for the model with four complexes and therefore, mathematically, the presence of four complexes is indicated. However, we already pointed out in one of our earlier publications[1] that the mathematical criterion in itself is not sufficient and should be sustained by spectroscopic arguments. In the case of the chloride system, for example, the observed coordinates of the isosbestic points, viz. 270 nm (3670 dm^3 mol cm^{-1}), 310 (3240), 360 (1120), 950 (112), are in excellent agreement with those calculated for the [1, 2, 3, 4] model: 270 nm (3600 dm^3 mol^{-1} cm^{-1}), 380 (3420), 360 (1130), 950 (112). The

Table 1. Overall stability constants, β_j, of chloro- and bromo-complexes for the [1, 2, 3] and [1, 2, 3, 4] models

$CuCl^+$	5.0×10^7	4.1×10^7
$CuCl_2$	7.2×10^9	1.2×10^{11}
$CuCl_3^-$	3.7×10^{10}	5.7×10^{12}
$CuCl_4^{2-}$	—	2.3×10^{13}
$\sigma_{UV\text{-}vis}$	0.0722	0.0498
σ_{IR}	0.1804	0.1706
σ_t	0.1335	0.1215
$CuBr^+$	2.0×10^8	2.5×10^9
$CuBr_2$	1.7×10^{10}	1.3×10^{12}
$CuBr_3^-$	6.5×10^{10}	3.4×10^{13}
$CuBr_4^{2-}$	—	1.2×10^{14}
$\sigma_{UV\text{-}vis}$	0.1335	0.0925
σ_{IR}	0.1522	0.1409
σ_t	0.1386	0.1073

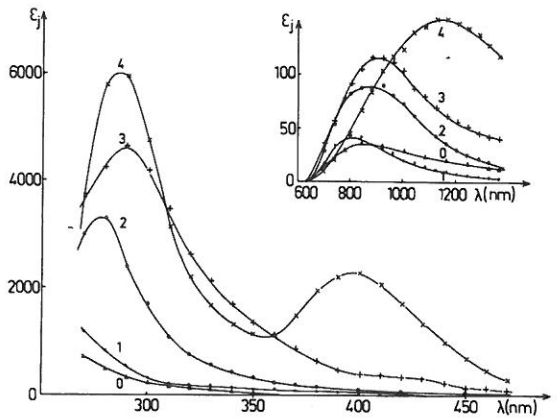


Fig. 3. Calculated electronic spectra of copper(II)-chloro-complexes in butan-1-ol for the model [1, 2, 3, 4].

isosbestic points pertain to the equilibrium between the trichloro and tetrachloro complexes.

The electronic spectra of individual species are shown in Figs 3 and 4 and the characteristic absorption bands are summarized in Table 2.

The tetrahalogenocuprates have their *d–d* transition bands at 1120 and 1200 nm and therefore have configurations of D_{2d} symmetry. We may recall here that in tetra-coordinated copper complexes *d–d* transitions at 1100 nm and above are due to structures of D_{2d} symmetry.

With the results of copper(II) halide complexes in butanol, we are now in a position to see clearly the different aspects of solvent effects on different properties of these complexes.

Table 3 gives the logarithms of overall stability constants, $\log \beta_j$, in the four alcohols and confirms our earlier assumption[3] that in a given solvent the bromides are generally more stable than the chlorides. Furthermore, it is seen that the stability of a given complex increases from methanol to butanol—the plot of $\log \beta_j$ against molecular weights of

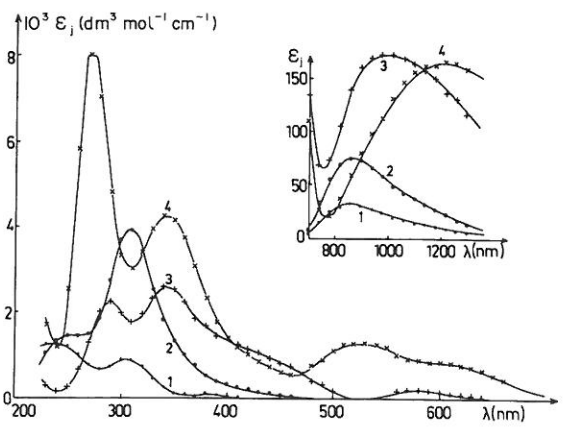


Fig. 4. Calculated electronic spectra of copper(II)-bromo-complexes in butan-1-ol for the model [1, 2, 3, 4].

Table 2. Characteristic absorption bands of all species present in the solution (sh = shoulder peak)

	Chloro-complexes λ_{max} (nm); ε_{max} ($dm^3\ mol^{-1}\ cm^{-1}$)	Bromo-complexes λ_{max} (nm); ε_{max} ($dm^3\ mol^{-1}\ cm^{-1}$)
Cu^{2+}	< 260 820 (30)	230 (1530) 820 (32)
CuX^+	≈ 265 (≈ 1200) 810 (48)	240 (1300) 306 (920) 860 (33)
CuX_2	280 (3300) 850 (93)	245 sh 310 (3925) 860 (75)
CuX_3^-	270 sh 290 (4630) 420 sh 910 (114)	290 (2450) 345 (2580) 460 sh 980 (172)
CuX_4^{2-}	290 (5950) 395 (2300) 1120 (160)	270 (8020) 340 (4220) 530 (1290) 600 (850) 1200 (167)

the alcohols is an increasing linear function [Fig. 5(a) and (b)]. This evolution is roughly true for the bromides but is very well respected in the chloride system. Theoretically, it is a very interesting relation which enables the prediction of the values of stability constants of copper(II) halide complexes in other alcohols, for example, pentanol, a very significant solvent, without undertaking (*a priori*) an experimental study. As far as we know this is the

Table 3. Logarithm of stability constants of chloro- and bromo-complexes of copper in different alcohols

Solvent	MeOH	EtOH	PrOH-2	BuOH-1
permittivity, ε_r	33	24	19.5	17
Molecular weight, Mol.wt	32	46	60	74
Chloro-complexes				
$\log \beta_1$	2.5	3.3	5.7	7.6
$\log \beta_2$	4.2	6.0	8.6	11.1
$\log \beta_3$	5.4	7.8	10.2	12.8
$\log \beta_4$	5.7	8.3	10.6	13.4
Bromo-complexes				
$\log \beta_1$	3.7	5.0	6.1	9.4
$\log \beta_2$	5.6	7.8	8.4	12.1
$\log \beta_3$	6.3	9.2	10.2	13.5
$\log \beta_4$	6.3	10.3	10.7	14.1

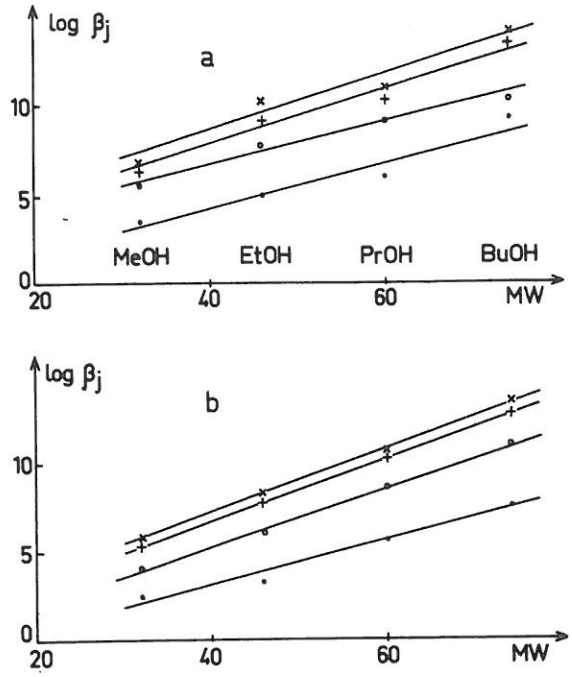


Fig. 5. Variation of the logarithm of the overall stability constants of the copper(II)-halogen-complexes with the molecular weight of the R—OH type solvents: (a) bromides and (b) chlorides.

first time that such a relation has been established in a specific type of solvent.

We may point out here that values of $\log \beta_j$ were plotted against molecular weights of the alcohols—a property which remains constant and unchanged. When dielectric constants of solvents are used care has to be taken to distinguish between the static dielectric constant, which is the permittivity of the pure solvent, and the variable dielectric constant, which changes with respect to the concentration of species in the solvent.[8] Nevertheless, a regular decrease of the stability of the complexes is observed with the dielectric constants of the solvents: the variation is close to linearity with dielectric constant values higher than 20.

The principal absorption bands of the complexes in butanol have been tabulated in Table 2. A comparison with those in other alcohols has shown no significant solvent effects on the characteristic absorption maxima in the UV and visible regions. All these absorptions in all the four alcohols can be located at ± 5 nm.

The structures of the tetra-coordinated complexes in the four alcohols can be compared to see the solvent effect on this property. The tetrachlorocuprate is known to exist under D_{4h} or D_{2d} configurations: the main difference between the two structures is that the ion of symmetry D_{4h} presents *d–d* transitions below 1100 nm, whereas the D_{2d} structure presents these bands at 1100 nm and above. This transition is at 1000 nm in methanol and at *ca* 1100 nm in the other three alcohols. Therefore, $CuCl_4^{2-}$ has a D_{4h} symmetry in methanol and a D_{2d} symmetry in the other three alcohols.

Demuynck *et al.*,[9] using LCAO–MO–SCF *ab initio* calculations in a thereotical study of bonding in $CuCl_4^{2-}$, showed that the configuration T_d is more stable, *ca* 72 kJ mol^{-1}, than the configuration D_{4h} and that the configuration D_{2d} is still more stable, by about 8 kJ mol^{-1}. The difference in energy calculated between these three configurations is, however, sufficiently low and the geometry of the molecule can easily be influenced by its surroundings.

In the solid state, $CuBr_4^{2-}$ has never been observed in D_{4h} symmetry, under normal conditions of temperature and pressure. Wang and Drickamer[10] have reported this structure but at pressures higher than 60 kbar (6.10^9 Pa). The tetrabromocuprate has, in all the alcohols, its *d–d* transitions at about 1100 and above and consequently exists exclusively in D_{2d} symmetry in solution.

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