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Communication

The dielectric constant and solvent effect on the stabilities of copper(II) chloro complexes

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The individually published results of the stability of copper(II) chloro complexes in various solvents have been assembled. The presence of four mononuclear complexes was postulated in the following solvents: ethanoic acid, tetrahydrofuran, trimethylphosphate, acetone, methanol, propylene carbonate and water, whereas dimethylformamide and dimethyl sulfoxide are characterized by the presence of only three complexes. The respective stability constants, β_j have been calculated and it is shown here that, for the protic solvents, $\log \beta_j$ is an inverse linear function of the dielectric constant, ε_r, of the solvent. However, for aprotic solvents, stability decreases with the increasing value of ε_r up to a certain value and then increases sharply from $\varepsilon_r \approx 45$. This sudden increase in the stability of complexes in propylene carbonate is explained on the basis of its low value for the molecular weight to dielectric constant ratio (μ_ε). This ratio should be given more importance in the interpretation of results correlating the stabilities with a physical parameter than the values of the dielectric constant alone, which are in themselves not static but a function of solution concentrations.

During the last fifteen years, a rigorous study of the copper(II) chloro complexes has been undertaken in different solvents. These studies determined the number of complexes formed in solution, their nature, their stability constants and their electronic spectra, and have been extended to other transition metals such as cobalt(II) and nickel(II)[1–3].

For the cupric ion, Table 1 summarises the results of the equilibrium studied: $Cu^{2+} + jCl^- \rightleftharpoons CuCl_j^{(j-2)-}$ where $j \leq 4$. The equilibrium is defined by the overall stability constant $\beta_j = [CuCl_j^{(j-2)-}]/[Cu^{2+}][Cl^-]^j$.

The results were obtained under the same experimental conditions, with the same methodology and using the same calculation program. Since we are comparing results in different solvents, the bibliography is limited to work carried out under similar conditions.

The presence of four successive mononuclear complexes was postulated in all the solvents studied except DMF and DMSO, where the absence of the second complex, $CuCl_2$, is accounted for by autocomplex formation leading to $CuCl^+$ and $CuCl_3^-$. The stability constants of all the species were derived using the same method of calculation and the solvent effect in certain categories discussed. A peculiar behaviour, however, is now reported and this, of course, became apparent only when all the individually published results were assembled.

A plot of $\log \beta_j$ *versus* the dielectric constant of the solvent, ε_r, shows that for protic solvents AcOH, MeOH and H_2O the stability diminishes with increasing value of the dielectric constant (Figure 1). $\log \beta_j$ is therefore a linear function of ε_r.

However, for the aprotic solvents studied: THF, TMP, Me_2CO, DMF, DMSO and propylene carbonate (PC), it can be discerned clearly that stability decreases until a certain value of dielectric constant, *ca.* 45 is reached, and then it increases sharply. This critical dip is interesting and can be further confirmed by studies of this system in solvents with ε_r values between 40 and 70.

This steep increase in the stability in PC has been reported by various authors even when the results were obtained by other experimental methods. Scharff[12], using potentiometric methods, reported the presence of three complexes in this medium and calculated their stability constants as $\log \beta_{CuCl^+} = 12.2$, $\log \beta_{CuCl_2} = 20.8$ and $\log \beta_{CuCl_3^-} = 27.4$. One of the reasons for these high values in PC is probably the low value of the ratio of its molecular weight to the dielectric constant: $\mu_\varepsilon = mw/\varepsilon_r = 102/69 = 1.48$. For all other aprotic solvents μ_ε has a higher value, *viz.* DMSO = 1.74; DMF = 2.03; Me_2CO = 2.77; TMP = 6.80 and THF = 9.49.

We believe that the ratio of the molecular weight to the dielectric constant should be given more importance *vis-à-vis* the dielectric constant of the solvent alone, which is not a static value for the purpose of generalisation. The molecular weight of the solvent, on the other hand, is an inherent and immutable property.

It may be recalled that the presence of ions in a solvent causes a decrease in the dielectric constant and therefore each solution containing a different ligand concentration has a different dielectric value. The reason for this decrease in the presence of ions is probably due to the restricted rotation of molecules in the vicinity of an ion, which hinders their orientation in the external field. The orientation of molecules can therefore no longer be controlled by the external field and the dielectric constant decreases with increasing concentration[13].

However, attempts to plot $\log \beta_j$ *versus* μ_ε yield a complex function, not at all like the simple linearity of $\log \beta_j$ *versus* ε_r. In conclusion, although studies on the basis of the dielectric constant of the solvent alone are simpler and give a fairly approximate idea of the stabilities of the complexes in different solvents, extreme care must be taken in generalising this behaviour.

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Table 1. Logarithm of stability constants of copper(II) chloro complexes identified in different solvents

Solvent	ε_r[a]	log β_1	log β_2	log β_3	log β_4	Ref.
Ethanoic acid (AcOH)	6.2	3.4	5.6	7.4	7.8	4
Tetrahydrofuran (THF)	7.6	11.8	20.3	23.9	25.7	5
Trimethylphosphate (TMP)	20.6	7.3	12.4	16.8	19.4	6
Acetone (Me_2CO)	21.0	8.4	14.5	19.9	21.5	7
Methanol (MeOH)	32.6	2.5	4.2	5.4	5.7	8
Dimethylformamide (DMF)	36.0	3.8	–	9.8	10.8	9
Dimethyl sulfoxide (DMSO)	45.0	3.0	–	6.9	7.5	10
Propylene carbonate (PC)	69.0	12.0	22.7	28.9	34.1	10
Water	78.5	0.60	0.67	0.29	−0.64	11

[a] Dielectric constant of the solvent.

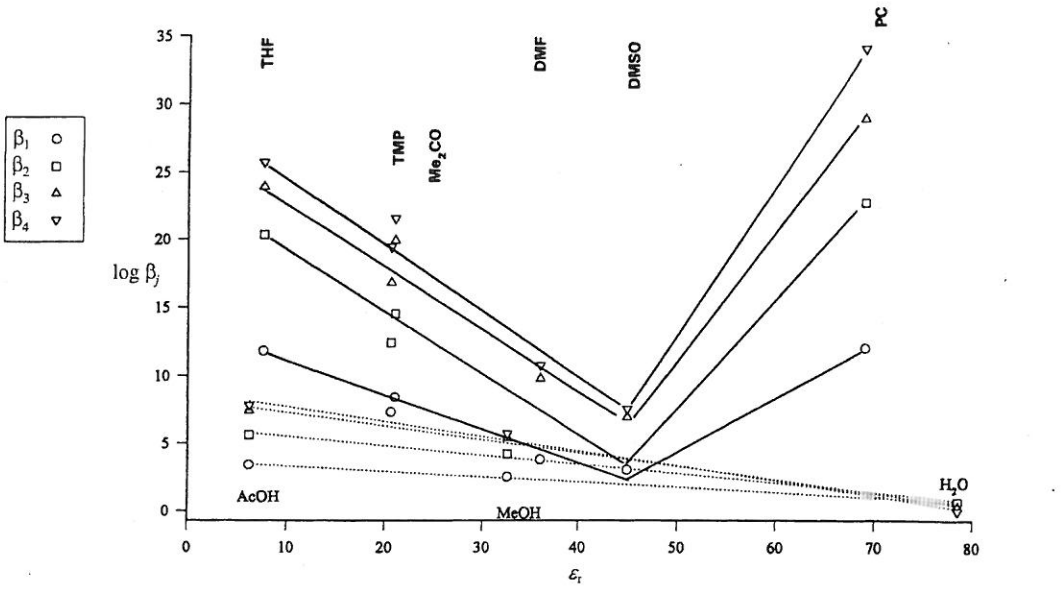


Figure 1. A plot of log β_j of the copper(II) chloro complexes *versus* the dielectric constant ε_r of the nine solvents studied. Dotted lines, protic solvents: solid lines, aprotic solvents.

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