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Table I. Consecutive Stability Constants and Ligand Effects for Copper(II) Chloro Complex Formation in 5 M Na(Cl,ClO$_4$) at 25 °C

$$L_{n,n+1} = \log (K_n/K_{n+1}) - S_{n,n+1}$$

$$S_{1,2} = S_{3,4} = 0.426 \qquad S_{2,3} = 0.352$$

ref	K_1	K_2	K_3	K_4	$L_{1,2}$	$L_{2,3}$	$L_{3,4}$
3, 4	4	1.2	0.42	0.12	0.097	0.104	0.118
2	1.5	0.42	0.14	0.036	0.127	0.125	0.164
1	2.49	0.46	0.79	0.028	0.307	−0.59	1.02

Table II. Molar Absorbance of CuCl$_2$ Solutions in the Blue Visible Region at ~25 °C[a]

	wavelength, nm				
	420	430	436	440	450
	I. C_{NaCl} = 4.00 M, C_{NaClO_4} = 1.00 M				
$\epsilon_\lambda{}^0$	548	380	308	263	168
ϵ_λ	24.4	15.8	12.0	9.95	5.96
α_4	0.044	0.042	0.039	0.038	0.035
	II. C_{NaCl} = 4.50 M, C_{NaClO_4} = 0.50 M				
ϵ_λ	28.0	18.2	14.2	11.9	7.32
α_4	0.051	0.048	0.046	0.045	0.044
	III. C_{NaCl} = 4.50 M, C_{NaClO_4} = 0.75 M				
ϵ_λ		20.0	15.6	13.2	8.13
α_4		0.053	0.051	0.050	0.048
	IV. C_{NaCl} = 5.35 M, C_{NaClO_4} = 0.00 M				
ϵ_λ		25.1	19.8	16.6	10.3
α_4		0.066	0.064	0.063	0.061
$\bar{n}$(IV–II)		1.91	1.84	1.80	1.81
$\bar{n}$(IV–III)		2.52	2.45	2.51	2.49

[a] Measured on a Cary 219 spectrophotometer with the experimental condition described previously.[2]

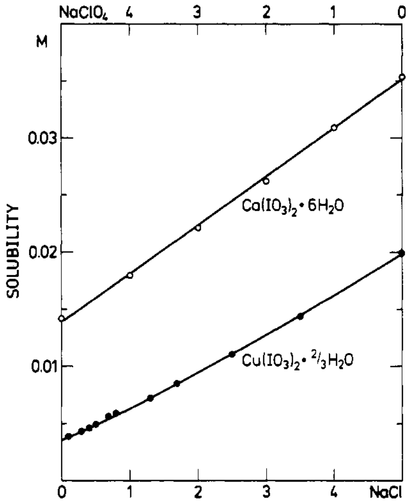

Figure 1. Solubility curve for Ca(IO$_3$)$_2$·6H$_2$O in 5 M Na(Cl,ClO$_4$) at 25 °C compared with the solubility curve for Cu(IO$_3$)$_2$ determined by Ramette and Fan[1] under the same conditions. Experimental conditions are as follows: The Ca(IO$_3$)$_2$·6H$_2$O employed was recrystallized and analyzed by iodate titration (purity 99.7 ± 0.2%). It was shaken with the salt medium in a thermostat, and equilibrium was found to be established after a few days. Powder X-ray diffractograms of the solid phases in equilibrium with 5 M NaCl and 5 M NaClO$_4$ that were isolated and dried at room temperature were identical with the diffractogram of a pure sample of Ca(IO$_3$)$_2$·6H$_2$O dried in a similar manner.

the tetraamine ion.[17] The spectrum of Cu(en)$_2$(H$_2$O)$^{2+}$ is practically the same in 5 M NaClO$_4$ as in dilute aqueous solution.

Registry No. Cu(IO$_3$)$_2$, 7789-80-2; NaCl, 7647-14-5; NaClO$_4$, 7601-89-0.

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(17) Romano, V., private communication.

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Copper(II) Complexes with Chloride Ion

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There are two reliable and independent equilibrium studies of copper(II) chloro complexes at ionic strength 5. One is a spectrophotometric study by Schwing-Weill,[1] later extended by Khan,[2] comprising a meticulous survey of 37 solutions ranging from 0.01 to 4.9 M sodium chloride, with measurements at 12 wavelengths in the UV and visible regions. By using an iterative computer algorithm, Khan and Schwing-Weill[3] found the best fit of the entire data set in terms of equilibrium constants for four successive complexes.

The other study,[4] from this laboratory, involved precise measurements of the solubility of copper iodate in a series of sodium chloride solutions up to 5 M. From ad hoc computer programs, the four β values were deduced to be significantly different from the spectrophotometric results, as shown in Table I.

Bjerrum and Skibsted opine[5] that both of these studies are lacking. They refer to the "suspiciously low value" for the molar absorptivity found by Khan and Schwing-Weill for the tetrachloro complex, and they suggest that the solubility approach suffers from medium effects as the solution composition varies from 5 M sodium perchlorate to 5 M sodium chloride. They have not addressed the obvious idea that the activity coefficients of the copper species in the spectrophotometric study are subject to exactly the same medium effects as in the solubility study. They have proposed[6] an alternative set of equilibrium constants (Table I) chosen to support their assumptions about the nature of copper(II) in the virtually nonaqueous medium of 6.2 M calcium chloride and their expectation of a nearly constant ligand effect.[11] We contend that such an approach is not a valid substitute for accurate experimental studies that can stand on their own.

At the time the solubility study was published, we were not yet appreciative of the power and value of nonlinear regression as a technique to deconvolute complex data. A good discussion of the application of this approach to chemical data has been given by Meites.[7] It includes proper weighting of data points and provides a least-squares fit based on the actual raw data. Because of Bjerrum and Skibsted's concern that the results from the solubility study show an unusual ligand effect, it seemed worthwhile to recalculate the solubility data by using nonlinear regression.

This technique involves making initial guesses of the four β values and using these to predict the solubility of copper iodate in each of the chloride solutions. The program then systematically refines the guesses until the fit is optimized. The resulting β values differ somewhat from those we published[4] and are to be preferred. They are 2.36 (0.07), 1.49 (0.19), 0.69 (0.13), and 0.055 (0.021) where the standard errors are shown in parentheses. The corresponding stepwise constants and calculated ligand effects are shown in Table I.

The next question was whether the spectrophotometric data of Khan[2] would yield different β values if subjected to nonlinear regression. At the wavelength of 230 nm Khan made measurements over the full range of chloride concentrations. Here it is necessary to make initial guesses of eight parameters for a given wavelength, the four β values and the four molar absorptivities of the complexes. The molar absorptivity of the uncomplexed copper ion is available from direct measurement in 5 M sodium

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Table I. Summary of K Values and Calculated Ligand Effects

$$K_n = [CuCl_n]/[CuCl_{n-1}][Cl^-]$$

$$L_{n,n+1} = \log (K_n/K_{n+1}) - \log \{(4 - n + 1)(n + 1)/(4n - n^2)\}$$

K_1	K_2	K_3	K_4	$L_{1,2}$	$L_{2,3}$	$L_{3,4}$	ref
4.0	1.2	0.42	0.12	0.10	0.10	0.12	2
1.5	0.42	0.14	0.036	0.13	0.13	0.15	6[b]
2.49	0.46	0.79	0.028	0.31	−0.59	1.02	4
2.36	0.63	0.46	0.080	0.15	−0.22	0.33	4[a]
2.31	0.65	0.38	0.082	0.12	−0.12	0.24	2[a]
2.3							8[a]

[a] As recalculated by nonlinear regression. [b] Ligand effects assigned, not calculated.

perchlorate. The nonlinear regression subroutine uses these parameters to predict the absorptivities. The best fit gave the β values 2.31, 1.49, 0.56, and 0.046, in very satisfying agreement with the results of our solubility study. The five corresponding absorptivities were 266 (fixed), 902, 1450, 1122, and 3372. As for the quality of the fit, the sum of the squares of the deviations in the absorptivities is only 20% as large as when Khan and Schwing-Weill's β values and absorptivities are used.

Further, as pointed out in our paper, a proper evaluation of the work by Ashurst and Hancock[8] also yields a value of 2.3 for K_1. Finally, it is worth repeating that the calorimetric study by Arnek[9] is not as well explained by Bjerrum and Skibsted's values as by those obtained by the solubility study. In conclusion, given these several agreeing experimental studies, there seems to be no point in further considering the alternative values of Bjerrum and Skibsted.

It remains to comment on the new data provided by Bjerrum and Skibsted on the solubility of calcium iodate in 5 M sodium chloride/perchlorate solutions. They state their opinion that the change in solubility is merely a medium effect, but had they applied the test of Harned's rule to their data, they would have seen that a plot of log S vs. chloride concentration is markedly curved, suggesting strongly that there is something happening in addition to a medium effect. Unfortunately, we cannot separate medium effects (activity coefficient changes) from effects due to complexing when dealing with such concentrated solutions. However, what they term "fictive" equilibrium constants can indeed be calculated from their solubility data, again by using nonlinear regression, and the results indicate the possibility of three very weak calcium chloride complexes, with β values of 0.68, 0.27, and 0.033. With so few points in their data set these results are tentative. Calcium chloride complexes have been proposed by Frantz and Marshall[10] on the basis of work at high temperature and pressure.

Bjerrum and Skibsted's contention that the Debye–Hückel theory indicates that the principle of constant ionic strength has little value in salt solutions more concentrated than 0.1 seems to ignore a great deal of data to the contrary and to misinterpret the limitations of the theory, which is capable of calculating activity coefficients reliably at low ionic strength but cannot make predictions of behavior in concentrated salt solutions.

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