DALTON
FULL PAPER

# Complexes of copper(I) with aromatic compounds in aqueous solutions

**Magal Saphier,**[a] **Ariela Burg,**[a] **Shlomit Sheps,**[a] **Haim Cohen**[ab] **and Dan Meyerstein** *[ac]

[a] *Chemistry Department, Ben-Gurion University of the Negev, Beer-Sheva, Israel.*
*E-mail: danmeyer@bgumail.bgu.ac.il*
[b] *Nuclear Research Centre Negev, Beer-Sheva, Israel.*
[c] *The College of Judea and Samaria, Ariel, Israel*

***Received 9th March 1999, Accepted 30th March 1999***

The apparent stability constants of the complexes of $Cu^+(aq)$ with several aromatic compounds, mainly substituted benzoic acids, were determined electrochemically. The results reveal that these complexes are surprisingly stable, $2.0 \le \log K \le 4.0$ at the $pK_a$ of the benzoic acids. The stability constants depend on the pH. This dependence is considerably stronger than that predicted from the $pK_a$ of the acids, suggesting that complexes of CuOH with the aromatic acids are also formed. Electron donating substituents increase the apparent stability constants. The results indicate that the complexes formed are due to d ⟶ π interactions between the copper d orbitals and the aromatic π system. The effect of $Cu^+(aq)$ on the $^1H$ NMR of benzoic acid supports this conclusion.

Copper(I) concentrations in aqueous solutions are limited due to two reasons: (1) the disproportionation reaction[1] (1) and

$$2Cu^+(aq) \rightleftharpoons Cu^{2+}(aq) + Cu^0 \qquad K = 5.38 \times 10^5\ dm^3\ mol^{-1} \quad (1)$$

(2) the low solubility product of CuOH or $Cu_2O$ and of other copper(I) compounds, *e.g.* copper(I) halides.[1,2] However copper(I) can be maintained at higher concentrations in aqueous solutions in the presence of suitable ligands: π acids, *e.g.* CO, $CH_3CN$, alkenes;[1,3] ligands which form $Cu^IL_2$ complexes whereas they form $Cu^{II}L_4$ complexes, due to entropic reasons, *e.g.* $L = NH_3$;[1,4] hydrophobic ligands, *e.g.* $CH_3N(CH_3)[CH_2CH_2N(CH_3)]_nCH_2CH_2N(CH_3)_2$ and $CH_3CN$.[5]

Copper(I) complexes are known to catalyse a variety of important organic processes.[6,7] Some of these, *e.g.* the Ullman reaction, are carried out in aqueous solutions, even in alkaline media.[7,8] This seems surprising as the concentration of $Cu^+(aq)$ under the experimental conditions should be extremely low.

Recent kinetic studies on Ullman reaction (2) suggested that

$$2\text{-}BrC_6H_4CO_2 \xrightarrow{Cu^I,\ H_2O} 2\text{-}HOC_6H_4CO_2^- + Br^- \qquad (2)$$

a complex between $Cu^I$ and the 2-bromobenzoate is a key intermediate in the process.[8] Indeed it is known that $Cu^I$ forms a complex with benzene and its crystal structure was reported.[9] Crystal structures of copper(I) carboxylates,[10] including the benzoate,[11] reveal, as expected, that the copper is co-ordinated to the oxygen of the carboxylate group. However in aqueous solutions, which have a high relative permittivity, the binding constant of $Cu^I$ to carboxylate is expected to be very small. Although in solid copper(I) fumarate spectral evidence indicates that the copper is co-ordinated to the oxygen, in aqueous solutions it is bound to the carbon–carbon double bond.[12]

It was therefore decided to try and determine the stability constants of the copper(I) complexes with several, water soluble, aromatic compounds.

## Experimental

### Materials

Solvents and reagents were reagent grade or better. Distilled water was further purified by passing through a Milli Q Millipore set-up (final resistivity >10 MΩ cm$^{-1}$). All the experiments were carried out at room temperature, 22 ± 2 °C.† The pH of all solutions was monitored with a Corning model 220 pH-meter, error ± 0.01 pH units, and the glass electrode was calibrated with standard buffers. All the experiments involving $Cu^I$ were carried out in strictly deaerated solutions, using the syringe technique.

### Spectroscopy

$^1H$ NMR spectra were recorded using a Bruker DPX 200 Hz spectrometer. Solutions in $D_2O$ containing 3% $CH_3CN$, $1 \times 10^{-3}$ mol dm$^{-3}$ benzoic acid and $1 \times 10^{-3}$ mol dm$^{-3}$ copper ions, $Cu(CH_3CN)_4PF_6$ or $CuSO_4$, at pH 4.7 were used. The UV-Vis spectra were recorded using a Hewlett-Packard 8452 diode array spectrophotometer. Special cells for anaerobic studies were used.

The concentration of $Cu^{2+}(aq)$ was determined spectrophotometrically by the addition of ammonia to form the complex $Cu(NH_3)_4{}^{2+}$ which has a molar absorption coefficient of 60 dm$^3$ mol$^{-1}$ cm$^{-1}$ at 604 nm.

### Determination of the stability constants of the copper(I) complexes

Two experimental approaches were utilized. Cyclic voltammograms and square wave data were recorded using an EG&G Princeton Applied Research Potentiostat and Galvanostat Model 263 driven by Model 270 electrochemistry software in connection with the hanging mercury drop electrode (HMDE) mode of Model 303A static mercury drop electrode (SMDE) and a Ag–AgCl reference electrode in a KCl–AgCl solution separated by a frit from the bulk solution. The solutions contained 0.2 mol dm$^{-3}$ $NaClO_4$, $1 \times 10^{-4}$ mol dm$^{-3}$ $CuSO_4$ (as small as possible concentration to prevent non-reproducible maximum spikes in the current) and $5 \times 10^{-4}$–0.05 mol dm$^{-3}$ of an aromatic compound. Fast scanning (5000–15000 mV s$^{-1}$) cyclic voltammograms and high frequency (600–1500 Hz) square wave (SW) voltammograms were recorded and the peaks attributed to the $Cu^{II/I}$ and $Cu^{I/0}$ redox processes deconvoluted using Cool software (mainly SW data were used as the derived half-wave potentials, $E_{\frac{1}{2}}$, are more reliable). Each system was

---

† The accuracy of the results obtained did not require the use of a more accurate temperature control.

studied at several concentrations of the aromatic solute; in the range $5 \times 10^{-4}$–$5 \times 10^{-2}$ mol dm$^{-3}$, and at several pH, from the p$K_a$ of the solute to pH 5.0; at lower pH the compounds are insoluble and at higher pH copper(II) precipitates and CuOH might be formed electrochemically (for 4-nitrophenol solutions at pH 6.0 had to be used). Plots of $E_{\frac{1}{2}}(\mathrm{Cu}^{I/0})$, after correcting for deviations of the $\mathrm{Cu}^{2+/0}$ potential from the standard one for each series of experiments, *vs.* log [L] yielded straight lines, see for example Fig. 3. From the intercepts of these lines, which all had slopes not far from −0.059 indicating the formation of a 1 : 1 complex *i.e.* $\mathrm{Cu^IL}$, the stability constants were calculated using eqn. (3) where $(E_{\frac{1}{2}})_{\mathrm{lit}}$ for $\mathrm{Cu^+(aq)} + e^- \longrightarrow \mathrm{Cu^0_{Hg}}$ is 0.386 V.[13]

$$\Delta E_{\frac{1}{2}} = (E_{\frac{1}{2}})_{\mathrm{exp}} - (E_{\frac{1}{2}})_{\mathrm{lit}} = -0.059 \log K_{\mathrm{Cu^+}} - 0.059 \log [\mathrm{L}] \quad (3)$$

Also plots of $E_{\frac{1}{2}}(\mathrm{Cu}^{II/I})$ *vs.* log [L] gave straight lines, Fig. 3, however these are more difficult to interpret as they have to be corrected for the stability constants of $\mathrm{Cu^{II}L}$, some of which are unknown, a process which decreases the accuracy of the results.

Fast scanning voltammetry is required as at normal scanning rates high concentrations of the ligands are required in order to obtain two well separated waves. Thus for example for maleic acid, for which $K = [\mathrm{Cu^IL}]/[\mathrm{Cu^+(aq)}][\mathrm{L}] = 1.06 \times 10^4$ dm$^3$ mol$^{-1}$ at pH 3.0, maleate concentrations $\geqslant 5 \times 10^{-2}$ mol dm$^{-3}$ are required in order to obtain two well separated waves.[12] However at high scan rates the disproportionation reaction is inhibited and two waves are observed at considerably lower ligand concentrations, see below. The solubility of the aromatic compounds in water is naturally limited.

In the second approach the effect of the aromatic ligand on the absorption of copper(I) fumarate at 346 nm was measured. The stability constant of the latter complex is known[12] and therefore by competition calculations the desired stability constants can be calculated, assuming that no mixed ligand complexes are formed. The reasonable agreement between the results obtained by these two approaches, see below, indicates that this assumption is correct. This technique is less accurate than the electrochemical one as dioxygen penetration, even at very low concentrations, affects the results significantly. Therefore this technique was used only to verify the electrochemical approach and to measure the stability constants of the phenol complex which could not be obtained electrochemically, probably due to adsorption to the mercury electrode, and of the pentafluorobenzoic acid complex which has the lowest stability constant.

The following experimental procedure was used: to a set of deaerated syringes containing known concentrations of $\mathrm{CuSO_4}$, fumarate, at a concentration high enough to ensure full comproportionation, the aromatic compound, at the desired pH, copper metal was added and the syringes were sealed and mixed for 24 h. The solution was then transformed into an anaerobic spectrophotometric cell and the optical density, at 346 nm was measured. The stability constants were calculated by comparing the optical density of samples containing no aromatic additive, which yield copper(I) fumarate, with those obtained in the presence of the aromatic additives. The calculations are based on eqns. (4)–(6) where L = fumarate, L′ = aromatic compound, $[\mathrm{Cu^I(L')}] = [\mathrm{Cu^I(L)}]^0 - [\mathrm{Cu^I(L)}]$, $[\mathrm{L}] = [\mathrm{L}]^0 - [\mathrm{Cu^I(L)}]$, $[\mathrm{L'}] = [\mathrm{L'}]^0 - ([\mathrm{Cu^I(L)}]^0 - [\mathrm{Cu^I(L)}])$, $[\mathrm{Cu^I(L)}] = A_{346}/\varepsilon_{346}(\mathrm{Cu^I(L)})$, $\varepsilon_{346}(\mathrm{Cu^I(L)}) = 1600$ dm$^3$ mol$^{-1}$ cm$^{-1}$ and $K_1 = 1.0 \times 10^4$ dm$^3$ mol$^{-1}$ at pH 3.0.[12]

$$\mathrm{Cu^+(aq)} + \mathrm{L} \rightleftharpoons \mathrm{Cu^I(L)} \quad K_1 = [\mathrm{Cu^I(L)}]/[\mathrm{Cu^+(aq)}][\mathrm{L}] \quad (4)$$

$$\mathrm{Cu^+(aq)} + \mathrm{L'} \rightleftharpoons \mathrm{Cu^I(L')} \qquad K_2 = [\mathrm{Cu^I(L')}]/[\mathrm{Cu^+(aq)}][\mathrm{L'}] \quad (5)$$

$$K_2 = K_1[\mathrm{Cu^I(L')}][\mathrm{L}]/[\mathrm{Cu^I(L)}][\mathrm{L'}] \quad (6)$$

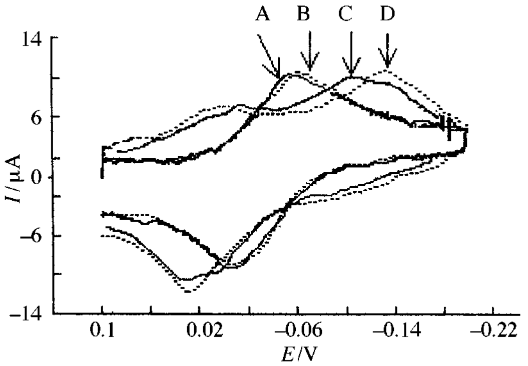

**Fig. 1** Cyclic voltammetry of $\mathrm{Cu^{II}}$ in the presence of 2-chlorobenzoic acid. Solution composition: $1 \times 10^{-4}$ mol dm$^{-3}$ $\mathrm{CuSO_4}$, 0.2 mol dm$^{-3}$ $\mathrm{NaClO_4}$, pH 4.0, scan rate 10000 mV s$^{-1}$ *vs.* Ag–AgCl. A, No additive; B, $5 \times 10^{-4}$ mol dm$^{-3}$; C, 0.02 mol dm$^{-3}$; and D, 0.05 mol dm$^{-3}$ 2-chlorobenzoic acid.

This technique has the drawback that dioxygen leaking into the syringe during the 24 h increases the measured optical density whereas a leak during the analytic stage decreases it. Therefore the accuracy of this technique is smaller than that of the electrochemical one.

## Results

Fast scanning cyclic voltammograms and high frequency square wave voltammograms of solutions containing 0.2 mol dm$^{-3}$ $\mathrm{NaClO_4}$, $1 \times 10^{-4}$ mol dm$^{-3}$ $\mathrm{CuSO_4}$ and $5 \times 10^{-4}$–0.05 mol dm$^{-3}$ of an aromatic compound were measured; typical results are shown in Figs. 1 and 2. The results clearly reveal that two well separated waves are obtained under these conditions in the presence of the aromatic compounds, the separation between the waves increasing with the concentration of the aromatic compound. These waves are attributed to the $\mathrm{Cu^{II/I}}$ and $\mathrm{Cu^{I/0}}$ redox processes.

Plots of $E_{\frac{1}{2}}(\mathrm{Cu^{I/0}})$ and of $E_{\frac{1}{2}}(\mathrm{Cu^{II/I}})$ *vs.* log[L′], where L′ is the aromatic compound, give straight lines, Fig. 3, as predicted. The slope of these lines should be $0.059(p - q)$ V for the redox processes $\mathrm{Cu}^n\mathrm{L'}_p + e^- \longrightarrow \mathrm{Cu}^{n-1}\mathrm{L'}_q + (p - q)\mathrm{L'}$. Therefore for the $\mathrm{Cu^{I/0}}$ process a slope of $\approx -0.059$ V is expected. The results always were somewhat smaller than predicted, *e.g.* −0.47 V in Fig. 3. This result seems to suggest that not all the interaction between the $\mathrm{Cu^0}$ formed and the aromatic compound is lost, a somewhat surprising result. However the results clearly demonstrate that a 1 : 1 complex is formed between $\mathrm{Cu^+(aq)}$ and all the aromatic compounds studied. The slopes of the lines at lower pH were usually considerably lower than 0.059 V/log[L′]; the source of this phenomenon is not clear. The slopes of the lines for the $\mathrm{Cu^{II/I}}$ process are significantly smaller, as expected, due to the formation of complexes between $\mathrm{Cu^{II}}$ and the aromatic acids.‡

The apparent stability constants of the $\mathrm{Cu^IL'}$ complexes were calculated from the intercepts of the straight lines obtained for the $\mathrm{Cu^{I/0}}$ processes. The results are summarised in Table 1.

In order to check the reliability of the technique used the stability constant of copper(I) maleate at pH 3.0 was measured in the frequency range 600–1000 Hz. The result, Table 1, log $K = 3.9 \pm 0.2$, is in excellent agreement with that measured at 60 Hz, log $K = 4.0$.[12] Also the results using the second

---

‡ One of the referees suggested that ternary complexes of the types 1 : 2 and 1 : 1 : 1 might be formed and affect the results. The results are in accord with the assumption that no 1 : 2 complexes are formed in these systems, consistent with expectations for a $d \longrightarrow \pi^*$ complex of $\mathrm{Cu^I}$. The pH effect on the apparent stability constants is in accord, see below, with the formation of 1 : 1 : 1 complexes of the aromatic compound; $\mathrm{Cu^I}$ and $\mathrm{OH^-}$. The limited pH range accessible for measurements and the limited accuracy of the results do not enable a detailed analysis of the stability constants of each species formed.

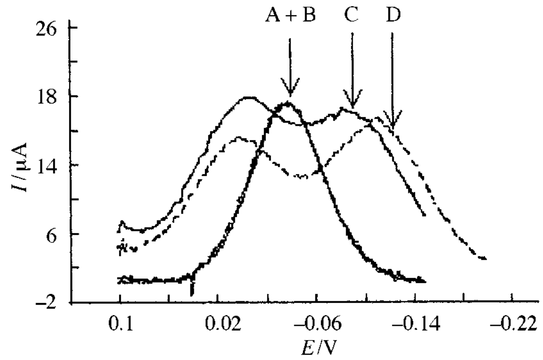

**Fig. 2** Square wave voltammetry of $Cu^{II}$ in the presence of 2-chlorobenzoic acid. Solution composition as in Fig. 1, frequency 800 Hz.

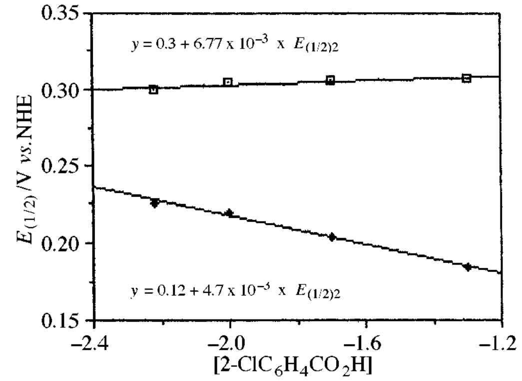

**Fig. 3** Plots of $E_{(1/2)2}(Cu^{I/0})$ and $E_{(1/2)1}(Cu^{II/I})$ (*vs.* NHE) against log [2-$ClC_6H_4CO_2H$]. $E_{(1/2)}$ values obtained by the square wave voltammetric experiments at 800 Hz, pH 5.0.

**Table 1** Stability constants of the copper(I) complexes

| Ligand | pH | log $K^a$ | p$K_a$ |
|---|---|---|---|
| Benzoic acid | 4.0 | 3.7 | 4.19 |
| | 4.0 | $4.1^b$ | |
| | 5.0 | 4.7 | |
| Salicylic acid | 3.0 | 2.9 | 2.97 |
| | 4.0 | 2.8 | |
| | 5.0 | 3.3 | |
| 2-Chloro-benzoic acid | 3.0 | 2.9 | 2.92 |
| | 4.0 | 3.7 | |
| | 5.0 | 4.5 | |
| 3-Bromobenzoic acid | 4.0 | 3.9 | 3.86 |
| | 5.0 | 5.6 | |
| 3-Methylbenzoic acid | 4.0 | 3.6 | 4.27 |
| | 5.0 | 4.7 | |
| 2-Methylbenzoic acid | 4.0 | 3.6 | 3.91 |
| | 4.0 | $4.2^b$ | |
| | 4.5 | 4.7 | |
| | 5.0 | 5.3 | |
| | 5.0 | $4.7^b$ | |
| Pentafluorobenzoic acid | 3.0 | $2.0^b$ | 1.8 |
| 4-Nitrophenol | 6.0 | 3.5 | |
| Maleate[c] | 4.0 | 3.9 | |
| Phenol[b] | 3.0 | $2.9^b$ | |

[a] Error limit ± 0.2. [b] Measured by the second approach, *i.e.* the effect of the aromatic ligand on the absorption of copper(I) fumarate at 346 nm,[12] error limit ± 0.5. [c] Previous result[12] log $K = 4.0$ is in full agreement with the present results.

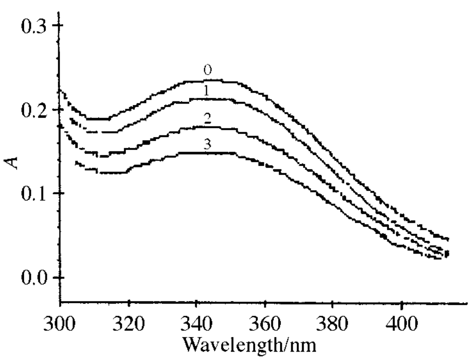

**Fig. 4** Effect of phenol on the yield of copper(I) fumarate. Deaerated solutions containing phenol, $1 \times 10^{-4}$ mol $dm^{-3}$ $CuSO_4$ and $5 \times 10^{-3}$ mol $dm^{-3}$ fumaric acid at pH 3.0 were stirred in the presence of copper metal for 24 h. The reference solution had the same composition but was not stirred in the presence of copper metal. Curves: 0, no phenol, $A_{364}$ 0.197; 1, $5 \times 10^{-3}$ mol $dm^{-3}$ phenol, $A_{346}$ 0.179; 2, $1 \times 10^{-2}$ mol $dm^{-3}$ phenol, $A_{346}$ 0.148; 3, $1.5 \times 10^{-2}$ mol $dm^{-3}$ phenol, $A_{346}$ 0.123.

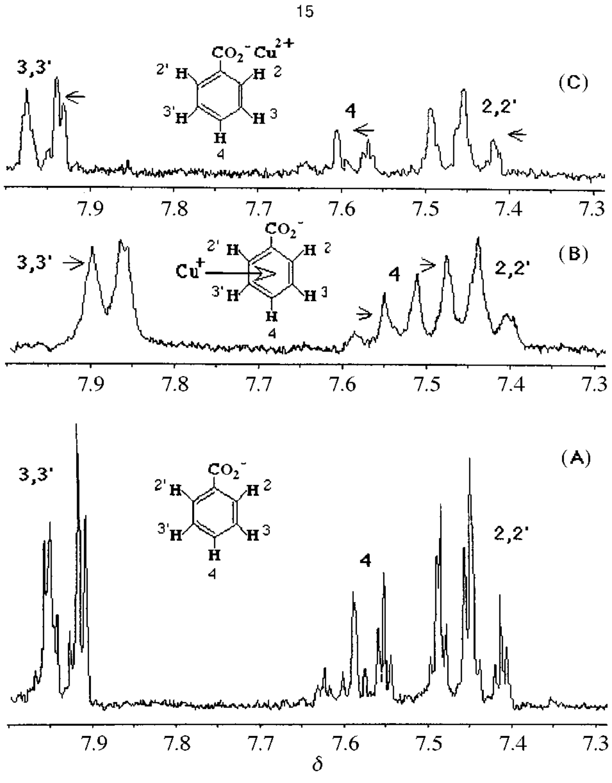

**Fig. 5** The effect of copper ions on the $^1H$ NMR of benzoic acid: (A), $D_2O$ solutions containing 3% $CH_3CN$, $1 \times 10^{-3}$ mol $dm^{-3}$ benzoic acid at pH 4.7; (B), same as (A) plus $1 \times 10^{-3}$ mol $dm^{-3}$ $Cu(CH_3CN)_4PF_6$, deaerated solution; (C) as (A) plus $1 \times 10^{-3}$ mol $dm^{-3}$ $CuSO_4$.

experimental approach, Table 1, confirm the validity of the electrochemical technique.

The apparent stability constants of the complexes of $Cu^+(aq)$ with benzoic acid, 2-methylbenzoic acid, pentafluorobenzoic acid and phenol were determined *via* the effect of the aromatic compound on the yield of copper(I) fumarate; typical results are presented in Fig. 4. The results, which are summarised in Table 1, for benzoic acid and 2-methylbenzoic acid are in agreement with those obtained electrochemically. The other two systems could not be studied using the electrochemical technique.

In order to verify the formation of complexes between $Cu^+(aq)$ and aromatic compounds, the effect of $Cu^+(aq)$ on the $^1H$ NMR spectrum of benzoic acid was measured; the spectra obtained are shown in Fig. 5. The results demonstrate that $Cu^+(aq)$ causes an upfield shift of the signals due to the aromatic hydrogens (on average 0.06 ppm for the *ortho* hydrogens, 0.01 ppm for the *meta* and 0.07 ppm for the *para*) whereas $Cu^{2+}(aq)$ causes a downfield shift of the same signals (on average 0.02 ppm for the *ortho*, 0.01 ppm for the *meta* and 0.03 for the *para* hydrogen).

## Discussion

The results clearly reveal that copper(I) forms in aqueous solutions surprisingly stable complexes with aromatic compounds. The apparent stability constants of the complexes are summarised in Table 1. It is of interest that the stability constant of the benzoate complex is considerably larger than that observed for the analogous copper(II) complex[14,15] and that of copper(II) acetate.[14] These observations show that the large stability constants of the copper(I) substituted benzoate complexes are due to a d $\longrightarrow$ π interaction between the $Cu^I$ and the aromatic ring and not to an electrostatic interaction with the carboxylate group. It is of interest that also the stability constant of silver(I) benzoate[16] is considerably larger than that of the acetate;[15] this result suggests that also the silver-benzoate is a d $\longrightarrow$ π complex.

Also the effect of $Cu^+(aq)$ on the $^1H$ NMR is in accord with the conclusion that the copper ion is bound to the aromatic ring and not to the carboxylate group. Thus copper(I) induces an upfield shift of the signals whereas copper(II), which is bound to the carboxylate, induces a downfield shift of the signals. The $^1H$ NMR spectra were recorded also at $Cu^I$: benzoic acid ratios considerably lower than 1:1 (results not shown). In these experiments only one set of signals was observed, though the shifts were smaller. These results indicate that the rate of formation and decomposition of the copper(I) benzoic acid/benzoate complex is fast on the timescale of the NMR measurement.

The apparent stability constants for most systems studied increase considerably with pH. (The case of salicylic acid is an exception and the effect could not be studied for phenol and 4-nitrophenol.) This effect is in most systems considerably larger than that which can be attributed to a larger stability constant for the anionic form than for the acidic form of the aromatic acids (thus for example for 2-chlorobenzoic acid the apparent stability constant of the complex increases by a factor of $\approx 40$ when the pH is raised from 3.0 to 5.0, whereas the concentration of the anion increases only by a factor of 2 by this pH change). It seems probable that CuOH is somehow involved in the complex formation in solutions with $pH \approx 5$. This uncertainty in the nature of the exact complex, or complexes, present in the solutions enables only the report of the apparent stability constants of the complexes.

When the apparent stability constants of the aromatic acids, at the pH of their $pK_a$ (derived by interpolation) in order to eliminate pH effects, are compared, Fig. 6, the results clearly point to a Hammett relation. The fact that an increased electron density on the ring stabilises the copper(I) complex is in accord with a recent conclusion[12] that the σ donating contribution is more important than the π* accepting contribution to the stability of these copper(I) complexes. This is probably due to the fact that $Cu^+(aq)$ is not a strong reducing agent.

Finally it should be pointed out that the results show that $Cu^+(aq)$ forms surprisingly stable d $\longrightarrow$ π* complexes with a variety of aromatic compounds in aqueous solutions. It was recently noted that interactions between copper(I) and aryl rings exist, though they are "somewhat of a novelty" and their nature is still not clear.[17] The finding that $Cu^+(aq)$ forms d $\longrightarrow$ π* complexes with a variety of aromatic compounds in aqueous solutions might be of importance in at least four ways. (1) The concentration of copper(I) species in aqueous solutions containing copper(II) salts in the presence of copper metal increases when aromatic compounds are added to the system. (2) If the copper(I) is bound mainly to one carbon–carbon bond of the aromatic ring and causes a severe geometric rearrangement of the ring as the crystal structure of $Cu^I(C_6H_6)^+$[9] and model calculations indicate, then its effect as a catalyst for a variety of processes is easier to understand. (3) In a variety of copper enzymes there are aromatic residues near the active site.[18] It might be speculated that in some of these enzymes interaction of $Cu^I$ with these residues contributes to the stability of their reduced form. (4) Recently Domenech *et al.*[19] have shown that macrocyclic ligands that contain aromatic rings stabilise $Cu^I$ in aqueous solutions. Their results reveal that methyl substituents increase the stability constants of these complexes in full agreement with the results presented herein. It is therefore proposed that, as their results show that the methyl substituents on the aromatic ring do not affect the stability of the copper(II) complexes, the properties of these ligands are due to the binding of $Cu^I$ to the π system of the aromatic ring and not to the hydrophobicity of these ligands as suggested.[19]

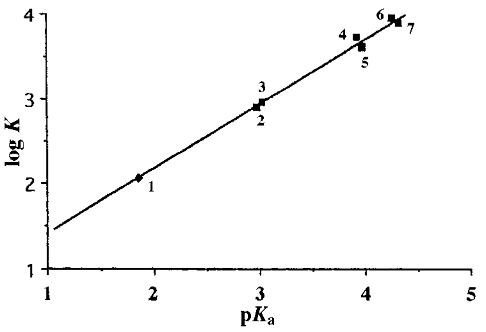

**Fig. 6** Dependence of log $K$ on the $pK_a$ of the aromatic acids. Values of log $K$ at the $pK_a$ of each acid are used. 1, $C_6F_5CO_2H$; 2, 2-$ClC_6H_4CO_2H$; 3, 2-$HOC_6H_4CO_2H$; 4, 2-$MeC_6H_4CO_2H$; 5, 3-$BrC_6H_4CO_2H$; 6, 3-$MeC_6H_4CO_2H$; 7, $PhCO_2H$.

## Acknowledgements

This study was supported in part by the Israel Science Foundation administered by The Israel Academy of Sciences and Humanities and by a grant from Budgeting and Planning Committee of The Council of Higher Education and Israel Atomic Energy Commission. D. M. wishes to express his thanks to Mrs. Irene Evens for her ongoing interest and support.

## References

1 L. Cravatta, D. Ferri and R. Palombari, *J. Inorg. Nucl. Chem.*, 1980, **42**, 593; F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn. Wiley-Interscience, New York, 1988, pp. 757 and 758.

2 *Handbook of Chemistry and Physics*, 74th edn., Chemical Rubber Publishing Co., Cleveland, OH, 1993–1994, pp. 4–57.

3 A. J. Parker, *Search*, 1973, **4**, 426.

4 T. F. Braish, R. E. Duncan, J. J. Harber, R. L. Steffen and K. L. Stevenson, *Inorg. Chem.*, 1984, **23**, 4072.

5 G. Golub, H. Cohen and D. Meyerstein, *J. Chem. Soc., Chem. Commun.*, 1992, 397; G. Golub, H. Cohen, P. Paoletti, A. Bencini, L. Messori, I. Bertini and D. Meyerstein, *J. Am. Chem. Soc.*, 1995, **117**, 8353.

6 A. Bruggink and A. Makillop, *Tetrahedron*, 1975, **31**, 2607; T. D. Tuong and M. Hida, *J. Chem. Soc., Perkin Trans. 2*, 1974, 676; A. J. Paine, *J. Am. Chem. Soc.*, 1987, **109**, 1496; H. Weingarten, *J. Org. Chem.*, 1954, **29**, 3624.

7 J. Lindley, *Tetrahedron*, 1984, **40**, 1433; A. A. Moroz and M. S. Shvartsberg, *Russ. Chem. Rev.*, 1974, **43**; T. Cohen and J. G. Tripak, *Tetrahedron Lett.*, 1975, 143; B. Liedholm, *Acta Chem. Scand.*, 1969, **23**, 3175; 1970, **25**, 113; 1976, **30**, 141.

8 M. Saphier, H. Cohen and D. Meyerstein, unpublished results.

9 R. W. Turner and E. L. Amma, *J. Am. Chem. Soc.*, 1963, **85**, 4046; 1966, **88**, 1877; H. Schmidbaur, W. Bublak, B. Huber, G. Reber and G. Muller, *Angew. Chem., Int. Ed. Engl.,*. 1986, **25**, 1089; C. J. Brown, P. J. McCarthy, I. D. Salter, K. P. Armstrong, M. Mcpartlin and H. R. Powell, *J. Organomet. Chem.*, 1990, **394**, 711; G. B. Ansell, M. A. Modrick and J. S. Bradley, *Acta Crystallogr., Sect. C*, 1984, **40**, 365.

10 M. G. B. Drew and D. A. Edwards, *J. Chem. Soc., Dalton Trans.*, 1977, 299.

11 D. A. Edwards and R. Richards, *J. Chem. Soc., Dalton Trans.*, 1973, 2463.

12 D. Meyerstein, *Inorg. Chem.*, 1975, **14**, 1716; N. Navon, A. Masarwa, H. Cohen and D. Meyerstein, *Inorg. Chim. Acta*, 1997, **261**, 29.

13 I. M. Kolthoff and J. J. Lingane, *Polarography*, 2nd edn., Interscience, New York, 1952, p. 211; J. F. Fischer and J. L. Hall, *Anal. Chem.*, 1967, **39**, 1550.

14 J. Bunting and K. Thong, *Can. J. Chem.*, 1970, **48**, 1654.

15 I. Leden, *Sen. Kem. Tidskr.*, 1942, **58**, 129.

16 D. G. Vartak and R. S. Shetiya, *J. Inorg. Nucl. Chem.*, 1967, **29**, 1261.

17 M. Mascal, J. Hansen, A. J. Blake and W. S. Li, *Chem. Commun.*, 1998, 355.

18 G. Maccarrone, G. Nardin, L. Randaccio, G. Tabbi, M. Rosi, A. Sgamellotti, E. Rizzarelli and E. Zangrando, *J. Chem. Soc. A*, 1966, 3449; W. E. DeWolf, Jr., S. A. Carr, A. Varrichio, P. J. Goodhart, M. A. Mentzer, G. D. Roberts, C. Southan, R. E. Dolle and L. I. Kruse, *Biochemistry*, 1988, **27**, 9093; G. Tian, J. A. Barry and J. P. Klinman, *Biochemistry*, 1944, **33**, 226.

19 A. Domenceh, J. V. Folgado, E. Garcia-Espana, S. V. Luis, J. M. Llinares, J. F. Miravet and J. A. Ramirez, *J. Chem. Soc., Dalton Trans.*, 1995, 541; A. Domenech, E. Garcia-Espana, V. Marcelino, B. Altava, S. V. Luis, J. F. Miravet, A. Bianchi and L. Ferrini, *Inorg. Chim. Acta*, 1996, **252**, 123.

*Paper 9/01834D*