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# Unexpected complexation behaviour of a sol–gel immobilised dye: the development of an optical copper(II) sensor†

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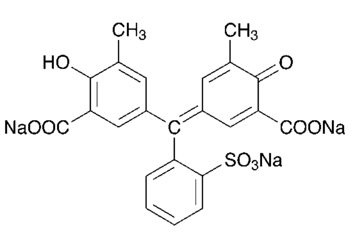
The metal-complexing dye Eriochrome Cyanine R (ECR) has been entrapped in sol–gel composites of good optical quality. The immobilisation of ECR had a dramatic effect on the complexation of metal ions. The strong colour change of aqueous ECR solutions, associated with the complexation of aluminium(III) ions, was not observed with ECR-containing composites. Instead a selectivity for copper(II) ions was found and a sensing system for these ions was developed. Thickness and pore structure were optimised to enhance sensitivity, lowering the detection limit for copper(II) ions to 0.1 ppm. The altered complexation behaviour is discussed in terms of effects of entrapment on entropy and enthalpy changes of complexation.

Porous glasses with high surface areas and good optical properties can be obtained by the hydrolysis of silicon alkoxides. This so-called sol–gel method has been shown to provide an elegant method for the immobilisation of various types of organic and inorganic molecules.[1] The principle of using sol–gel technology in the construction of optical sensors was already demonstrated in 1990,[2] and sol–gel derived sensing systems have been reported for a wide range of analytes in both gaseous[3] and aqueous solution phases.[4] Currently recognised advantages of sol–gel entrapment of analytical reagents include: immobilisation with minimal leaching; uniform dispersal of reagent, facilitating access by analytes; use of pore size selectivity to protect reagents while allowing ingress of analytes; the pre-concentrating effect associated with adsorption onto the porous silica surface, and the good optical quality of many sol–gel composites. However, the active role of the sol–gel matrix in influencing the thermodynamics of reactions of entrapped reagents has not yet been recognised or exploited. In this paper we report remarkable changes in the selectivity of the metal-complexing reagent Eriochrome Cyanine R (ECR) **1** following sol–gel entrapment. These suggest that the role of the sol–gel matrix may be much more extensive than previously recognised, affording wide prospects for control of sensitivity and selectivity *via* designed modification of the sol–gel entrapment matrix.



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Eriochrome Cyanine R was first suggested as a reagent for aluminium ions by Eegriwe in 1929.[5] Its complexation with $Al^{III}$ ions, producing a red–violet colour, has been considered the most sensitive spectrophotometric method for the determination of aluminium.[6] An optical sensor based on diffuse reflectance spectrophotometry has recently been developed using ECR immobilised on a styrene–divinylbenzene cross-linked copolymer.[7] The present work was originally motivated by the desire to monitor the concentration of aluminium ions in surface waters, which prompted us to investigate the construction of a sensor using entrapped ECR in a porous glass matrix.

## Experimental

### General

Absorption spectra were recorded on a Pye Unicam SP 500 series 2 UV–VIS spectrophotometer, pH measurements were carried out using a Griffin pH meter model 80. Surface area determination was performed using a Micromeritics High Speed Surface Area Analyser. The samples were degassed at 100 °C. Pore size distributions were determined by thermoporometry using a Perkin Elmer DSC 7 differential scanning calorimeter following literature procedures.[8] Tetramethoxysilane was obtained from Lancaster Synthesis, ECR was obtained from Fisons.

### Preparation of the sol–gel glasses

Tetramethoxysilane (TMOS) (2.5 ml) was dissolved in 3.0 ml of ethanol containing $5\times10^{-8}$–$10^{-6}$ mol ECR. Water (1.6 ml) was added, followed by two drops of aqueous HCl (final pH 5.0). The mixtures were stirred for 30 min and transferred to petri dishes which had been made hydrophobic by treatment with dichlorodimethylsilane. The dishes were sealed and after 3 days, in which gelation occurred, controlled evaporation of the solvent was allowed by making pinholes in the covers of the petri dishes. More pinholes were made after shrinkage of the gels could be observed (generally 6–7 days after preparation). On the tenth day the gels were placed in an oven whose temperature was slowly raised from 25 to 50 °C by 5 °C $h^{-1}$, and left at this temperature for 4 days. After cooling down to room temperature they were left for 2 days before the covers were removed. The obtained composites containing 0.04–0.87 µmol ECR per g were left to age for another two weeks before use.

### Metal ion complexation

Complexation experiments were carried out by placing composites containing 0.17 µmol ECR per g in a standard 1 cm cuvette, which had been masked in order to match the shape of the composite. In order to maintain constant analyte

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concentration, the cuvette was placed in a beaker containing 50 ml of metal ion solutions of which the pH had been adjusted to the desired value. The cuvette was taken out at set time intervals and absorption spectra recorded using the metal ion solution as a reference.

## Results and Discussion

### Metal ion complexation in ECR-containing composites

TMOS-based sol–gel composites were prepared containing varying amounts of ECR. Remarkably, the surface areas of glasses depended on the presence of the dye, but not so much on its concentration (Fig. 1). When gels which had not been allowed to age were placed in water, leaching of the dye into the aqueous phase was observed. No leaching was observed, however, from gels which had been aged for 2 weeks.

The glasses showed an absorption band with a $\lambda_{max}$ of approximately 500 nm which broadened with increasing ECR concentrations, possibly due to aggregation of the dye. The absorption spectra of the glasses showed a dependence on the pH of the aqueous phase, similar to that observed for aqueous ECR solutions. Consequently, the pH of each solution was adjusted to a controlled value (4.5 or 6.5, see Fig. 2 and 3, reference 9).

Pieces of glass containing 0.17 μmol ECR per g were immersed in 0.1 mM solutions of $KAl(SO_4)_2$. Surprisingly, only minor changes in the absorption spectra could be observed after exposure for 20 days. This cannot be explained by complexation of $Al^{III}$ ions with the surface Si—OH groups of the composite since 3,5,7,2′,7′-pentahydroxyflavone-containing composites (prepared in the same manner as the ECR-containing composites) showed a fluorescence signal upon exposure to $Al^{III}$ concentrations as low as 10 ppm.[10]

In order to check whether entrapped ECR molecules are still able to complex metal ions the composites were exposed to 1.0 mM solutions of $Cr^{III}$, $Fe^{III}$, $Zr^{II}$, $Be^{II}$ and $Cu^{II}$ ions,[9] which are known to form complexes with ECR in aqueous solution. Only copper, and to a lesser extent beryllium ions, gave rise to a change in the absorption spectrum of the entrapped ECR (Fig. 2). This indicates that immobilisation in a sol–gel matrix still allows ECR to form complexes with metal ions, but that it substantially modifies the selectivity of the complexation reaction.

The most likely origin of this changed selectivity lies in the effect small pores have on the thermodynamics of the complexation reaction. Since aluminium ions, due to their 3+ charge, have large negative entropies of hydration, the Gibbs free energy of complex formation largely depends on the entropy term, *i.e.* on the release of water molecules during complex formation.[11] Due to the confinement of water molecules in small pores in the silica matrix, however, the translational entropy associated with their release is not fully developed. In addition, the hydrogen bonding of water to Si—OH groups on the pore walls alters the solvent structure, as is shown for example by melting point depression.[12] As is well known in conventional solution thermodynamics, modified solvent structure affects both the enthalpy and entropy changes associated with reactions. Small pores may furthermore affect the complexation reaction by restricting the conformational motions of the ligand, altering the mode of complexation, or by isolating the ligands so that the required stoichiometry for complex formation cannot be achieved.

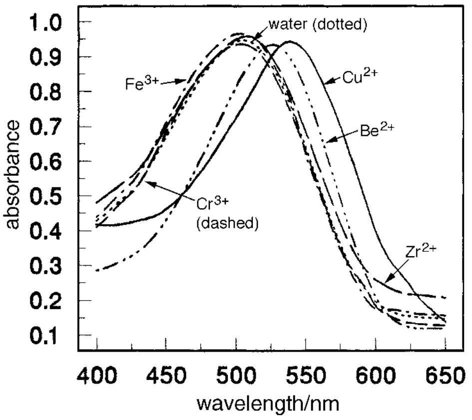

**Fig. 2** Spectra of an ECR sol–gel composite in 1 mM aqueous solutions of different metal ions at pH 4.5 (solid line, $Cu^{2+}$; dash-triple dot, $Be^{2+}$; long dash, $Zr^{2+}$; dash-dot, $Fe^{3+}$; medium dash, $Cr^{3+}$; dotted line, water)

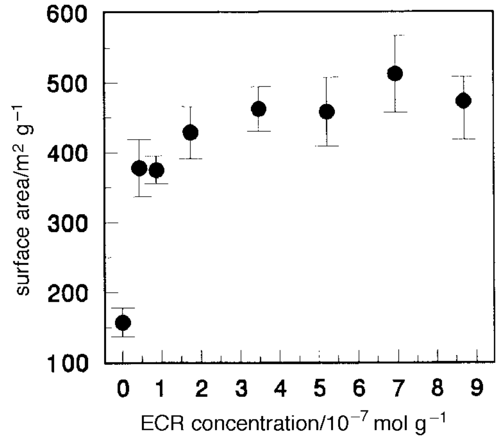

**Fig. 1** Variation of sol–gel composite surface area as a function of Eriochrome Cyanine R (ECR) concentration

### The development of a copper(II) sensor

As was described above, the sol–gel entrapped ECR showed selectivity for copper(II) ions and to a lesser extent for beryllium(II) ions. However, when the metal ion concentrations were lowered to 0.1 mM only a response for copper ions was observed (Fig. 3). This prompted us to develop the ECR-containing composite into a $Cu^{II}$ sensing system.

The selectivity of the system was further checked by exposing the glasses to solutions of metal ions which are known to have a complexation behaviour similar to that of copper(II) [*e.g.* $Ni^{II}$, $Co^{II}$ and $Zn^{II}$], or which are present at high concentrations in surface waters (*viz.* $Ca^{2+}$ and $Mg^{2+}$). No interference was found from 1.0 mM solutions of these divalent cations. Furthermore, the response of ECR-containing glasses was found to be anion-independent since identical results were obtained from 1.0 mM solutions of copper(II) chloride, sulfate and acetate.

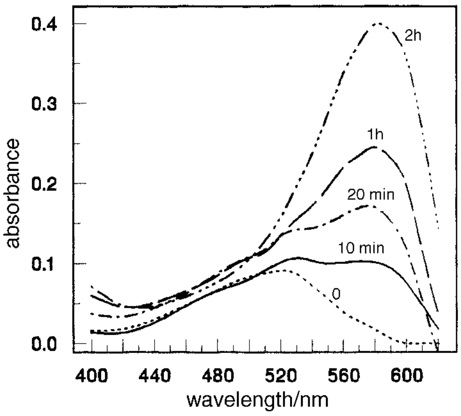

**Fig. 3** Spectra of an ECR sol–gel composite after exposures for different times to 0.1 mM $Cu^{2+}$ in aqueous solution at pH 6.5

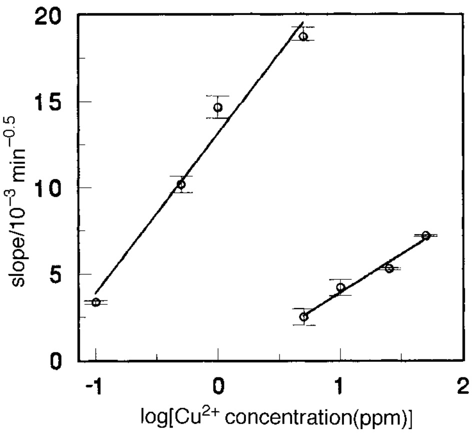

**Fig. 4** Dependence of the diffusion rate of $Cu^{2+}$ ions into an ECR sol–gel composite [as measured from the slopes of plots of absorbance *vs.* $\surd$(time)] on $Cu^{2+}$ concentration in the surrounding solution (upper line for 'thin' sample, lower line for 'thick' sample—see text)

Attempts to reverse the complex formation by washing with dilute aqueous sulfuric acid were unsuccessful, indicating that the copper(II) ions are irreversibly bound in the matrix. Due to the irreversibility of complex formation, the rate of colour development rather than the intensity of the final colour was used to measure the copper(II) concentration. The linear relation between the amount of complex formed (as judged from the optical absorbance) and the square root of time, indicates that the complexation of the metal ions inside the sol–gel matrix follows Fick's law of diffusion. The rates of optical absorption change were not influenced by earlier exposures of the glasses to different (either higher or lower) concentrations of copper(II) ions and a calibration curve could be obtained over a concentration range of 5–50 ppm (Fig. 4).

The detection limit in a diffusion controlled system, as described here, depends on the length of the diffusion path through the silica matrix, *i.e.* on the pore size distribution in the material and on the thickness of the glass. Efforts made to increase the pore size of the materials only led to leaching of ECR, even if prolonged ageing times were applied. Surprisingly, the reduction of the thickness of the glasses by half resulted in a seven-fold increase of the rate of optical absorption change for a concentration of 5 ppm. The consequent decrease in response time allowed the detection of concentrations as low as 0.1 ppm (Fig. 4).

The decreased diffusion pathlength due to the two-fold reduction of the sample thickness cannot account for this seven-fold reduction of the response time, suggesting that changes in the porosity of the material may also contribute to this effect. Similar specific surface areas were obtained for samples of both thicknesses, but thermoporometry[8] revealed that the pore size distribution indeed was altered upon changing the thickness of the sample. The original materials had a trimodal pore size distribution containing small pores with an average diameter of 7 nm, another type of small pore of approximately 8–15 nm diameter, and mesopores with diameters of 25–75 nm [Fig. 5(a)]. The new materials again showed two types of small pores, one with an average diameter of 10 nm, the other with diameters between 10 and 25 nm, but the larger mesopores were absent [Fig. 5(b)]. These differences in pore size distribution were attributed to modified drying characteristics imposed by the change in the thickness of the sample.

Assuming that the bigger mesopores found in the original sample are not a rate limiting factor in the diffusion of copper ions, the diffusion of the analyte will only depend on transport through small pores. The increased rate of absorption change is therefore probably a consequence of the fact that in the thin glass the second type of small pores have a significantly larger diameter.

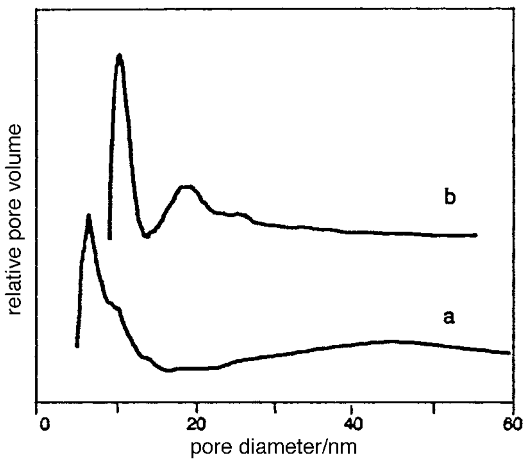

**Fig. 5** Pore size distributions determined by thermoporometry for (a) 'thick' and (b) 'thin' samples (see text)

## Conclusions

ECR entrapped in sol–gel composites displays a selectivity for complexing metal ions which is different from that of the dye in solution. The entrapment in small pores may affect the complexation reaction by changing the translational entropy of the release of water from the hydration sphere of the metal ion, as well as by modifying the enthalpy changes of the complexation reaction *via* changes in the solvent structure through the hydrogen bonding between the water molecules and the surface Si—OH groups. Control over the pore size distribution in the composites may therefore be used to tune the selectivity of complex formation. In a similar manner the enthalpy of the reaction could be changed by modifying the surface of the pore walls (by the use of different precursors, *e.g.* methyltrimethoxysilane). This again may be used to optimise the sensing properties of sol–gel composites. Work focussed on the tuning of the selectivity of sensors by modification of the sol–gel matrix is in progress.

### References

1 B. Dunn and J. I. Zink, *J. Mater. Chem.*, 1991, **1**, 903.
2 R. Zusman, C. Rottman, M. Ottolenghi and D. Avnir, *J. Non-Cryst. Solids*, 1990, **122**, 107.
3 A. K. McEvoy, C. McDonagh and B. D. MacCraith, *J. Sol–Gel Sci. Technol.*, 1997, **8**, 1121.
4 C. Rottman, M. Ottolenghi, R. Zusman, O. Lev, M. Smith, G. Gong, M. L. Kargan and D. Avnir, *Mater. Lett.*, 1992, **13**, 293; M. Tsionsky and O. Lev, *Analyst*, 1993, **118**, 557.
5 From W. E. Trun, *Anal. Chem.*, 1948, **20**, 1117.
6 Z. Marcenko, *Spectrophotometric Determination of Elements*, Halsted Press, Wiley, Chichester, 1976.
7 M. Ahmad and R. Narayanaswamy, *Anal. Chim. Acta*, 1994, **291**, 255.
8 J. F. Quinson and M. Brun, *J. Non-Cryst. Solids*, 1988, **99**, 151; M. Brun, A. Lallemand, J. F. Quinson and C. Eyraud, *Thermochim. Acta*, 1977, **21**, 59; K. Ishikiriyama, M. Todoki and K. Motomura, *J. Colloid Interface Sci.*, 1995, **171**, 92.
9 These experiments were carried out at pH 4.5 due to the limited solubility of some of the salts at neutral pH.
10 S. A. Wallington, T. Labayen, A. Poppe, N. A. J. M. Sommerdijk and J. D. Wright, *Sensors Actuators B*, 1997, **38–39**, 48.
11 For example: $\Delta G$, $\Delta H$ and $T\Delta S$ for an $Al^{III}$–EDTA complex at 20 °C have been determined to be $-90.7$, $+52.8$ and 143.6 kJ mol$^{-1}$, respectively (cited in C. S. G. Phillips and R. J. P. Williams, *Inorganic Chemistry*, Oxford University Press, Oxford, 1966, vol. II, p. 83).
12 J. F. Quinson and M. Brun, *Characterisation of porous solids*, Elsevier, Amsterdam, 1988.

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