

Acoustic wave sensor for barium based on poly[Ni(*salen*)(crown)] recognition chemistry

Magda Martins,^a Cristina Freire^{*a} and A. Robert Hillman^{*b}

^a CEQUP/Departamento de Química, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal. E-mail: acfreire@fc.up.pt; Fax: (+) 351 226082959; Tel: (+) 351 226082890

^b Department of Chemistry, University of Leicester, Leicester, UK LE1 7RH. E-mail: arh7@leicester.ac.uk; Fax: (+) 44 116 252 3789; Tel: (+) 44 116 252 2144

Received (in Cambridge, UK) 28th November 2002, Accepted 20th December 2002

First published as an Advance Article on the web 10th January 2003

Interfacial recognition of barium by a crown ether receptor is quantified using an acoustic wave sensor, and the isotherm characteristics rationalized in terms of solution complexation chemistry and polymer materials properties.

Molecular recognition is the critical step of innumerable chemical processes. In particular, the associated selectivity and sensitivity are crucial for sensing applications at solid/fluid interfaces¹ based on electroactive polymers,² Langmuir–Blodgett and self-assembled monolayers,³ ‘molecular gates’ in insulating monolayers,⁴ oligonucleotides⁵ and antibody–antigen systems.⁶ Here we report recognition of an electroinactive metal ion (barium) by a crown ether receptor bound within a Ni(*salen*)-based electroactive polymer matrix immobilized on an acoustic wave resonator. We combine the selectivity of recognition chemistry with the sensitivity and *in situ* capability of the quartz crystal microbalance (QCM) to provide a simple route to quantitation; this contrasts with the qualitative detection capabilities commonly reported for other detection strategies, such as voltammetry. Further, parameterization of the underlying binding chemistry—through an isotherm—provides mechanistic insights and criteria for analytical exploitation.

Polymers prepared by oxidative polymerization of Ni(*salen*) monomers in low coordinating solvents are novel materials,⁷ since they contain discrete localized redox entities (Ni centers) and delocalized redox units (the extended conjugated system in the polymerized *salen*-type ligand). We recently envisaged the possibility of functionalizing them with crown ethers (Fig. 1) to generate polymers able to recognize metal ions. Our present objective is to combine the molecular recognition properties of these crown ether functionalized polymers with the *in situ* transduction capabilities of acoustic wave devices. Sensors based on acoustic wave devices⁸ are presently finding wide applicability. In liquid media the frequency response of thickness shear mode (TSM) resonators (such as QCM) can provide information on the exchange of species between the sensor surface and the bathing fluid in electrochemical,⁹ DNA or enzyme biochemical,¹⁰ and analytical¹¹ contexts. For an acoustically thin (‘rigid’) film, the resonant frequency decreases linearly with coupled mass and the device is a gravimetric sensor.⁸ When loaded with thicker and/or softer films, the device is a viscoelastic sensor; interpretation is more complex, but is well-defined¹² and sensitivity may be enhanced.⁸ In either case, the sensitivity to surface population changes is *ca.* 1–100 pmol. Selectivity may be achieved *via* a surface coating possessing appropriate recognition characteristics.

The first issue is whether to interpret the TSM resonator response in gravimetric or viscoelastic terms. Fig. 2 shows

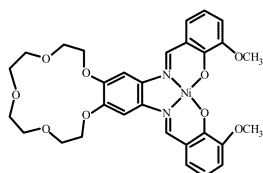


Fig. 1 [Ni(3-MeOsalo-phen-b-15-c-5)].

diagnostic¹² crystal admittance spectra for a poly[Ni(3-MeOsalo-phen-b-15-c-5)]-loaded resonator exposed first to TEAP/CH₃CN background electrolyte, then to Ba(ClO₄)₂ solution.† Our aim is to quantify the response to Ba²⁺.

Since the resonant admittance for the polymer-loaded resonator is slightly lower than that for the bare resonator, the film is not perfectly elastic (‘rigid’). Using a recently published theoretical model^{12a} and procedure^{12b} we can now determine shear moduli, $G = G' + jG''$. We obtain a storage modulus, $G' \approx 5 \times 10^8$ dyn cm⁻² and a loss modulus, $G'' \approx 3 \times 10^8$ dyn cm⁻², characteristic of a lossy viscoelastic material just below the viscoelastic/glassy borderline. The response to Ba²⁺ injection is a decrease in resonant frequency but little change in peak shape, consistent with a change (increase) in inertial mass but not viscoelastic properties. Strictly, for a near-rigid film, the minor effect of viscoelasticity can be described by a correction,¹³ $7.8\Delta R_3(G'/G'')$ (where ΔR_3 is the film contribution to the resonant resistance), to the Sauerbrey equation.⁸ For films deposited using < 25 cycles, this is a < 3% effect, which we ignore.

We can now explore the response to small Ba²⁺ injections. Using the Sauerbrey equation,⁸ we converted the observed equilibrium (long time scale) frequency change to a film mass change, Δm (ng). The objective is a relationship between surface population and solution phase Ba²⁺ concentration (*c*). The simplest model relating the fractional coverage of sites (θ) to the solution concentration is the Langmuir isotherm. In gravimetric terms this is:

$$\frac{1}{\Delta m} = \frac{1}{\Delta m_\infty} + \frac{1}{\Delta m_\infty Kc} \quad (1)$$

where Δm_∞ is the limiting mass increase at high concentration and K (mol⁻¹ dm³) is the absorption equilibrium constant.

Fig. 3 shows a plot of $1/\Delta m$ vs $1/c$ for a typical acoustically thin film: linearity is consistent with eqn. (1). The intercept (high concentration limit) yields $\Delta m_\infty = 1585$ ng. Interpretation of this sample-specific value in terms of material properties requires correlation with the number of receptor sites in the film, which may be assayed coulometrically or by a combined gravimetric/ICP analysis. The frequency shift asso-

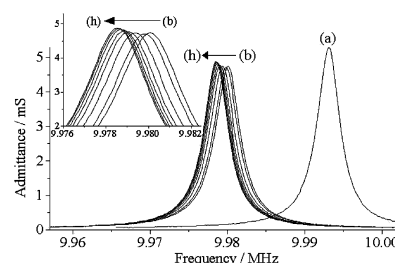


Fig. 2 *In situ* TEAP/CH₃CN TSM admittance spectra for: (a) bare Pt electrode, (b)–(h) poly[Ni(3-MeOsalo-phen-b-15-c-5)], $\Gamma = 77.1$ nmol cm⁻² (thickness 0.71 μ m), loaded Pt electrode. Spectrum (b) is prior to Ba²⁺ injection; spectra (c)–(h) acquired sequentially following Ba²⁺ injection.

ciated with film deposition corresponds to the mass of 'polymer + included electrolyte solution'; for the film of Fig. 3, this is 6.94 μg . ICP Ni assay of a number of films shows that the polymer content corresponds to 0.46 (± 0.05) of the total film mass. In the present case (using the molar mass of monomer), the surface population of crown ether receptors is 5.12 (± 0.56) nmol. The effective molar mass of barium species per crown ether site is thus 309 (± 27) g mol^{-1} —remarkably similar to the molar mass of $\text{Ba}(\text{ClO}_4)_2$, 336 g mol^{-1} . Given that Ba^{2+} entry into the film must, on electroneutrality grounds, be accompanied by an equivalent amount of ClO_4^- , the inescapable conclusion is that the effective entering species is ' $\text{Ba}(\text{ClO}_4)_2$ '; any solvent entry associated with solvation is apparently balanced by solvent expulsion on volume grounds. This is an interesting and surprisingly simple result, with consequences for the interpretation of the partition characteristics.

We now turn to the Langmuir plot slope, $(K \Delta m_\infty)^{-1}$. Using Δm_∞ from the intercept, we obtain $K = 1.56 \times 10^5 \text{ mol}^{-1} \text{ dm}^3$, *i.e.* the solution concentration required for 50% site occupancy, $c_{1/2} = 1/K = 6.4 \mu\text{mol dm}^{-3}$. Since analogous values have not been reported for barium uptake into other crown ether receptors immobilized in polymer films on surfaces, direct comparisons are not possible. However, it is interesting to compare K with complexation constants for barium and other ions by solution phase crown ethers. Binding constants for Li^+ , Na^+ and K^+ by pendant crown ether functionalities (with 5 or 6 O-donors) on thiophene-based monomers (precursors to polythiophene conducting polymers) are in the range 0.75–2.8 $\times 10^5 \text{ mol}^{-1} \text{ dm}^3$.¹⁴ Values of K for Ba^{2+} complexation with 'isolated' (non-*salen*-bonded) benzo-15-crown-5 and the monomeric [$\text{Ni}(\text{3-MeOsalo phen-b-15-c-5})$], respectively, are 2.25 $\times 10^5$,¹⁵ and 1.66 $\times 10^4 \text{ mol}^{-1} \text{ dm}^3$.¹⁶

To compare these solution binding constants with that found here for the poly[$\text{Ni}(\text{3-MeOsalo phen-b-15-c-5})$] film, we assume: (i) the intrinsic process of complexation is the same in both cases, and is described by an equilibrium constant K^* and Gibbs energy change $\Delta G_{\text{complex}}$, and (ii) the effective value, K , determined in the present work represents a combination of the underlying complexation process and the energy, ΔG_{trans} , associated with transfer of $\text{Ba}(\text{ClO}_4)_2$ from the solution into the film. It follows that:

$$\Delta G_{\text{complex}} = -RT \ln(K^*) = -RT \ln(K) - \Delta G_{\text{trans}} \quad (2)$$

Thus, the values of the measured film and solution complexation constants will differ according to the Gibbs energy of transfer, *i.e.* $\ln[K/K^*] = -\Delta G_{\text{trans}}/RT$.

Assuming the same underlying complexation chemistry and energetics in the film and solution implies that uncomplexed barium ions in the film and in solution experience similar local environments; since the film solvent content is greater than 50%, this is plausible. Although the energy change in transferring between two identical environments will be zero, the film must be allowed to swell to accommodate the entering $\text{Ba}(\text{ClO}_4)_2$. This involves work, given by the product of the elastic component of the film modulus (G') and the volume change, *i.e.*, in the absence of volume of mixing effects, the molar volume of $\text{Ba}(\text{ClO}_4)_2$, $V_m \approx 105 \text{ cm}^3 \text{ mol}^{-1}$. We obtain $G' V_m \approx 5.4 \text{ kJ mol}^{-1}$. Equating this with ΔG_{trans} , the predicted

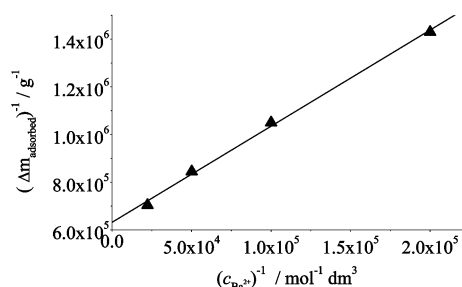


Fig. 3 Langmuir plot for $\text{Ba}(\text{ClO}_4)_2$ uptake; $\Gamma = 39.5 \text{ nmol cm}^{-2}$ (thickness 0.36 μm).

ratio $K/K^* \approx 0.10$, in gratifying agreement with the experimental ratio of 0.11. Although K for the polymer film is apparently close to that for the isolated crown in solution, this appears to be fortuitous, since attachment of the crown to the *salen* moiety (in solution) decreases K by an order of magnitude.

To conclude, the concept of encapsulating solution complexation chemistry within a polymer immobilized on an acoustic wave sensor has been implemented quantitatively. We have correlated the interfacial complexation chemistry with that of solution analogs—invariably the starting point for interfacial design—and rationalized the effect of polymer immobilization of the receptor in materials properties terms. We chose to illustrate the method for an electroinactive metal ion (barium), but the strategy is generic. Manipulation of (aza)-crown ether chemistry can provide selectivity for other metals, and application of a potential control function will allow simultaneous acoustic and electrochemical determinations of electroinactive and electroactive ions; in the latter case, the conducting polymer spine will provide facile charge transport.

EPSRC (GR/N00968) and FCT-Lisboa (project POCT/32831/QUI/2000) provided financial support. Dr C. Sousa provided nickel monomer. MM thanks FCT for a fellowship.

Notes and references

† Preparation of monomer (4',5'-bis(3-methoxysalicylideneimine)-benzo[15-crown-5] nickel(II)), [$\text{Ni}(\text{3-MeOsalo phen-b-15-c-5})$] is described elsewhere.¹⁶ Poly[$\text{Ni}(\text{3-MeOsalo phen-b-15-c-5})$] films were deposited potentiodynamically (between -0.3 V and 1.2 V (SCE); 0.02 V s^{-1}) on polished Pt electrodes supported on 10 MHz AT cut quartz crystals (piezo/electroactive area 0.20 cm^2) using 0.1 mmol dm^{-3} monomer in 0.1 mol dm^{-3} tetraethylammonium perchlorate/ CH_3CN solutions. Polymer coverage was controlled by the number of voltammetric deposition cycles; over the range 1–100 cycles, coulometric assay shows polymer coverage (Γ) increases linearly by 1.2 nmol cm^{-2} per cycle. After electropolymerization, the modified electrodes were rinsed thoroughly with dry CH_3CN , immersed in 0.1 mol dm^{-3} TEAP/ CH_3CN solutions and kept at -0.3 V . Incremental injections of known volumes of $\text{Ba}(\text{ClO}_4)_2$ were made and the crystal admittance response monitored.¹² No attempt was made to control mass transport; thus, to assess equilibration times for films of varying thickness, measurements spanned a range from seconds to hours.

- L. M. Goldendberg, M. R. Bryce and M. C. Petty, *J. Mater. Chem.*, 1999, **9**, 1957–1974.
- D. T. McQuade, A. E. Pullen and T. M. Swager, *Chem. Rev.*, 2000, **100**, 2537–2574.
- P. D. Beer, N. Berry, M. G. B. Drew, O. D. Fox, M. E. Padilla-Tosta and S. Patell, *Chem. Commun.*, 2001, 199–200.
- R. M. Crooks, *ChemPhysChem.*, 2001, **2**, 644–654.
- H. Matsuno, H. Furusawa and Y. Okahata, *Chem. Commun.*, 2002, 470–471.
- X. Su, S. F. Y. Li and S. J. O'Shea, *Chem. Commun.*, 2001, 755–756.
- (a) M. Vilas Boas, C. Freire, B. de Castro, P. A. Christensen and A. R. Hillman, *Inorg. Chem.*, 1997, **36**, 4919–4929; (b) M. Vilas Boas, C. Freire, B. de Castro, P. A. Christensen and A. R. Hillman, *Chem. Eur. J.*, 2001, **7**, 139–150.
- D. S. Ballantine, R. M. White, S. J. Martin, A. J. Ricco, E. T. Zellers, G. C. Frye and H. Wohltjen, *Acoustic Wave Sensors*, Academic Press, San Diego, 1997.
- I. Jureviciute, S. Bruckenstein and A. R. Hillman, *Phys. Chem. Chem. Phys.*, 2000, **2**, 4193–4198.
- A. Janshoff, H.-J. Galla and C. Steinem, *Angew. Chem., Int. Ed.*, 2000, **39**, 4004–4032.
- N. G. Karousos and M. Reddy, *Analyst*, 2002, **127**, 368–372.
- (a) H. L. Bandey, S. J. Martin, R. W. Cernosek and A. R. Hillman, *Anal. Chem.*, 1999, **71**, 2205–2214; (b) A. R. Hillman, A. Jackson and S. J. Martin, *Anal. Chem.*, 2001, **73**, 540–548.
- A. R. Hillman and S. Ramirez, *J. Electrochem. Soc.*, 1998, **145**, 2640–2647.
- H. K. Youssoufi, A. Yassar, S. Baiteche, M. Hmyene and F. Garnier, *Synth. Met.*, 1994, **67**, 251–254.
- J. Massaux, G. Roland and J. Desreux, *Inorg. Chim. Acta*, 1982, **60**, 129–133.
- C. Sousa, P. Gameiro, C. Freire and B. de Castro, manuscript in preparation.