

## **The binding of phosphonic acids at aluminium oxide surfaces and correlation with passivation of aluminium flake**

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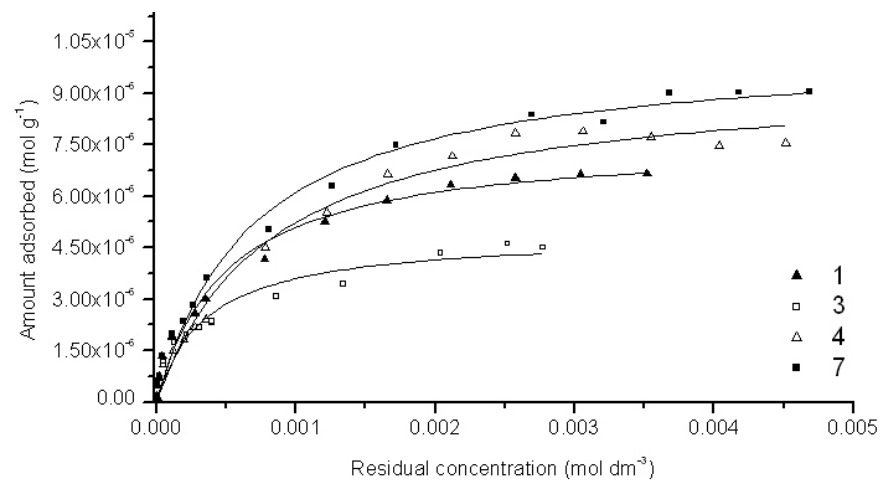
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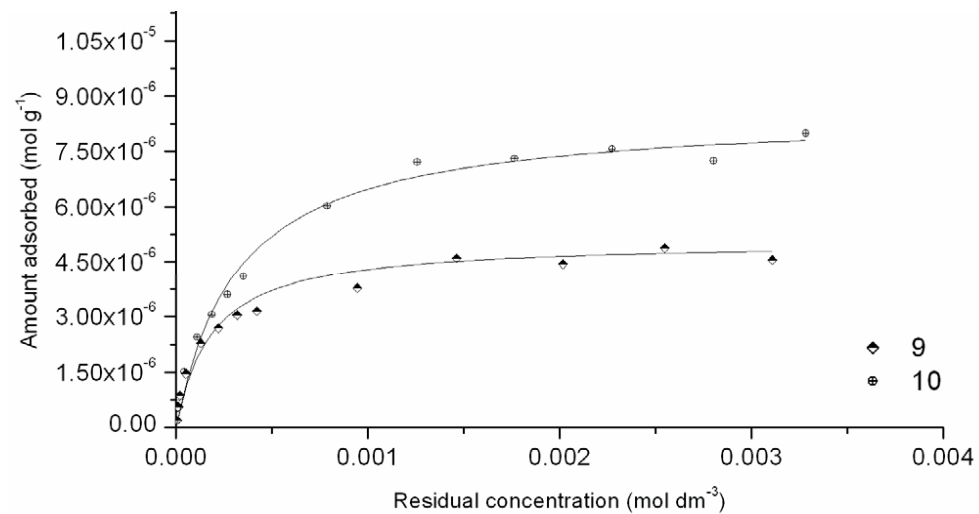
Data for Figure 3 – isotherms of 1, 3, 4 and 7 (pH 8.5, 25 °C)



| Compound 1                                     |                                        | Compound 3                                     |                                        | Compound 4                                     |                                        | Compound 7                                     |                                        |
|------------------------------------------------|----------------------------------------|------------------------------------------------|----------------------------------------|------------------------------------------------|----------------------------------------|------------------------------------------------|----------------------------------------|
| Residual concentration (mol dm <sup>-3</sup> ) | Amount adsorbed (mol g <sup>-1</sup> ) | Residual concentration (mol dm <sup>-3</sup> ) | Amount adsorbed (mol g <sup>-1</sup> ) | Residual concentration (mol dm <sup>-3</sup> ) | Amount adsorbed (mol g <sup>-1</sup> ) | Residual concentration (mol dm <sup>-3</sup> ) | Amount adsorbed (mol g <sup>-1</sup> ) |
| 3.03E-06                                       | 1.61E-07                               | 3.03E-06                                       | 1.78E-07                               | 4.32E-06                                       | 1.43E-07                               | 3.03E-06                                       | 1.74E-07                               |
| 9.16E-06                                       | 4.76E-07                               | 1.14E-05                                       | 4.78E-07                               | 1.05E-05                                       | 4.92E-07                               | 9.36E-06                                       | 5.19E-07                               |
| 1.86E-05                                       | 7.12E-07                               | 2.32E-05                                       | 6.98E-07                               | 1.99E-05                                       | 7.47E-07                               | 1.90E-05                                       | 7.78E-07                               |
| 4.09E-05                                       | 1.34E-06                               | 5.06E-05                                       | 1.18E-06                               | 4.66E-05                                       | 1.08E-06                               | 4.19E-05                                       | 1.33E-06                               |
| 1.12E-04                                       | 1.91E-06                               | 1.26E-04                                       | 1.75E-06                               | 1.21E-04                                       | 1.49E-06                               | 1.11E-04                                       | 1.99E-06                               |
| 2.74E-04                                       | 2.60E-06                               | 2.16E-04                                       | 1.97E-06                               | 1.98E-04                                       | 1.81E-06                               | 1.91E-04                                       | 2.36E-06                               |
| 3.52E-04                                       | 3.01E-06                               | 3.07E-04                                       | 2.17E-06                               | 2.74E-04                                       | 2.17E-06                               | 2.67E-04                                       | 2.82E-06                               |
| 7.77E-04                                       | 4.16E-06                               | 4.00E-04                                       | 2.30E-06                               | 3.55E-04                                       | 2.42E-06                               | 3.58E-04                                       | 3.62E-06                               |
| 1.21E-03                                       | 5.27E-06                               | 3.97E-04                                       | 2.35E-06                               | 7.83E-04                                       | 4.51E-06                               | 8.06E-04                                       | 5.04E-06                               |
| 1.66E-03                                       | 5.88E-06                               | 8.60E-04                                       | 3.08E-06                               | 1.22E-03                                       | 5.52E-06                               | 1.26E-03                                       | 6.30E-06                               |
| 2.11E-03                                       | 6.34E-06                               | 1.34E-03                                       | 3.44E-06                               | 1.66E-03                                       | 6.64E-06                               | 1.72E-03                                       | 7.49E-06                               |
| 2.58E-03                                       | 6.54E-06                               | 2.04E-03                                       | 4.36E-06                               | 2.12E-03                                       | 7.17E-06                               | 2.69E-03                                       | 8.38E-06                               |
| 3.05E-03                                       | 6.64E-06                               | 2.52E-03                                       | 4.61E-06                               | 2.58E-03                                       | 7.83E-06                               | 3.21E-03                                       | 8.16E-06                               |
| 3.52E-03                                       | 6.66E-06                               | 2.77E-03                                       | 4.51E-06                               | 3.06E-03                                       | 7.89E-06                               | 3.68E-03                                       | 9.01E-06                               |
| -                                              | -                                      | -                                              | -                                      | 3.55E-03                                       | 7.72E-06                               | 4.18E-03                                       | 9.03E-06                               |

|   |   |   |   |          |          |          |          |
|---|---|---|---|----------|----------|----------|----------|
| - | - | - | - | 4.04E-03 | 7.49E-06 | 4.68E-03 | 9.05E-06 |
| - | - | - | - | 4.52E-03 | 7.54E-06 | -        | -        |

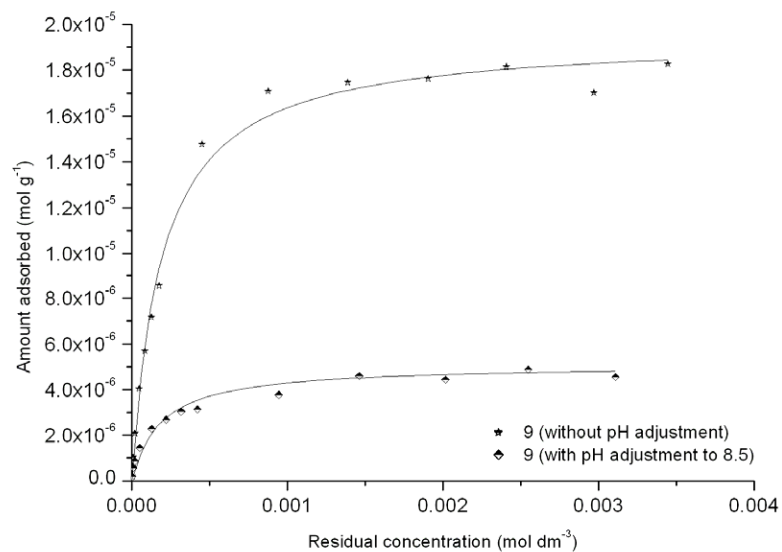
Data for Figure 4 – isotherms of **9** and **10** (pH 8.5, 25 °C)



| Compound <b>9</b>                              |                                        | Compound <b>10</b>                             |                                        |
|------------------------------------------------|----------------------------------------|------------------------------------------------|----------------------------------------|
| Residual concentration (mol dm <sup>-3</sup> ) | Amount adsorbed (mol g <sup>-1</sup> ) | Residual concentration (mol dm <sup>-3</sup> ) | Amount adsorbed (mol g <sup>-1</sup> ) |
| 3.19E-06                                       | 1.92E-07                               | 3.45E-06                                       | 1.70E-07                               |
| 9.84E-06                                       | 5.66E-07                               | 1.00E-05                                       | 5.23E-07                               |
| 1.98E-05                                       | 8.72E-07                               | 1.86E-05                                       | 8.13E-07                               |
| 5.08E-05                                       | 1.46E-06                               | 4.25E-05                                       | 1.50E-06                               |
| 1.28E-04                                       | 2.28E-06                               | 1.08E-04                                       | 2.44E-06                               |
| 2.20E-04                                       | 2.69E-06                               | 1.86E-04                                       | 3.05E-06                               |
| 3.17E-04                                       | 3.04E-06                               | 2.67E-04                                       | 3.60E-06                               |
| 4.21E-04                                       | 3.14E-06                               | 3.51E-04                                       | 4.10E-06                               |
| 9.44E-04                                       | 3.78E-06                               | 7.88E-04                                       | 6.02E-06                               |
| 1.46E-03                                       | 4.60E-06                               | 1.26E-03                                       | 7.21E-06                               |
| 2.02E-03                                       | 4.44E-06                               | 1.77E-03                                       | 7.31E-06                               |
| 2.55E-03                                       | 4.88E-06                               | 2.27E-03                                       | 7.56E-06                               |

|          |          |          |          |
|----------|----------|----------|----------|
| 3.11E-03 | 4.56E-06 | 2.80E-03 | 7.25E-06 |
| -        | -        | 3.28E-03 | 7.99E-06 |

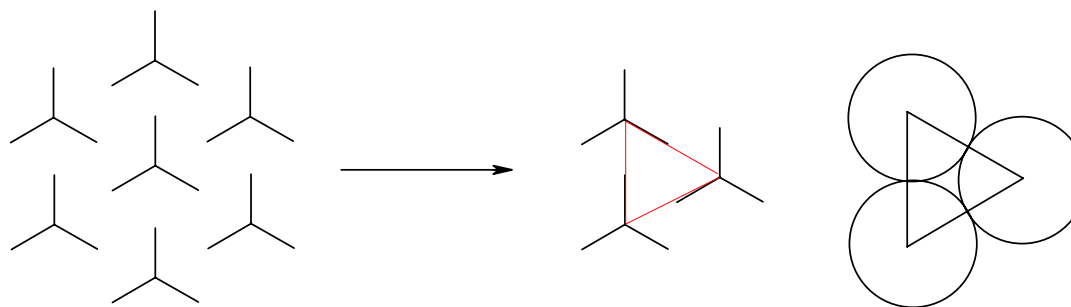
Data for Figure 5 – isotherms of **9** (with and without pH adjustment), pH 8.5 and pH 3.0, 25 °C



| Compound <b>9</b>                                 |                                           | Compound <b>9</b><br>(without pH adjustment)      |                                           |
|---------------------------------------------------|-------------------------------------------|---------------------------------------------------|-------------------------------------------|
| Residual concentration<br>(mol dm <sup>-3</sup> ) | Amount adsorbed<br>(mol g <sup>-1</sup> ) | Residual concentration<br>(mol dm <sup>-3</sup> ) | Amount adsorbed<br>(mol g <sup>-1</sup> ) |
| 3.19E-06                                          | 1.92E-07                                  | 2.16E-06                                          | 2.06E-07                                  |
| 9.84E-06                                          | 5.66E-07                                  | 6.13E-06                                          | 6.27E-07                                  |
| 1.98E-05                                          | 8.72E-07                                  | 1.01E-05                                          | 1.04E-06                                  |
| 5.08E-05                                          | 1.46E-06                                  | 2.04E-05                                          | 2.08E-06                                  |
| 1.28E-04                                          | 2.28E-06                                  | 4.63E-05                                          | 4.04E-06                                  |
| 2.20E-04                                          | 2.69E-06                                  | 8.43E-05                                          | 5.69E-06                                  |
| 3.17E-04                                          | 3.04E-06                                  | 1.26E-04                                          | 7.17E-06                                  |
| 4.21E-04                                          | 3.14E-06                                  | 1.75E-04                                          | 8.56E-06                                  |
| 9.44E-04                                          | 3.78E-06                                  | 4.51E-04                                          | 1.48E-05                                  |
| 1.46E-03                                          | 4.60E-06                                  | 8.76E-04                                          | 1.71E-05                                  |
| 2.02E-03                                          | 4.44E-06                                  | 1.39E-03                                          | 1.75E-05                                  |
| 2.55E-03                                          | 4.88E-06                                  | 1.90E-03                                          | 1.76E-05                                  |
| 3.11E-03                                          | 4.56E-06                                  | 2.41E-03                                          | 1.82E-05                                  |
| -                                                 | -                                         | 2.97E-03                                          | 1.70E-05                                  |
| -                                                 | -                                         | 3.45E-03                                          | 1.83E-05                                  |

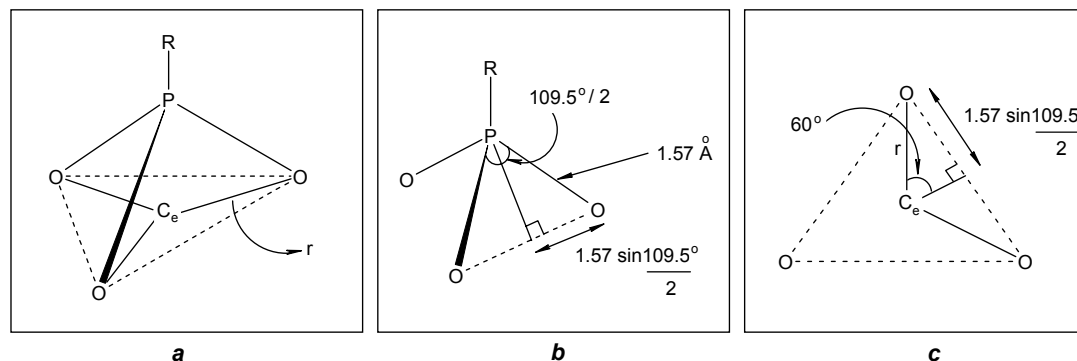
*Calculations and discussion associated with Figure 5 and Table 4*

If ligands are close packed on the surface, the theoretical area of each molecule can be estimated by assuming initially that the nuclei of the oxygen atoms of the head group ( $\text{PO}_3^{2-}$  or  $\text{PO}_3\text{H}^-$ ) lie on the circumference of a circle radius,  $r$ . Allowance will then need to be made for the van der Waals radii of the deprotonated oxygen atoms or likely contact radius for oxygen atoms forming H-bonds (Figure A).



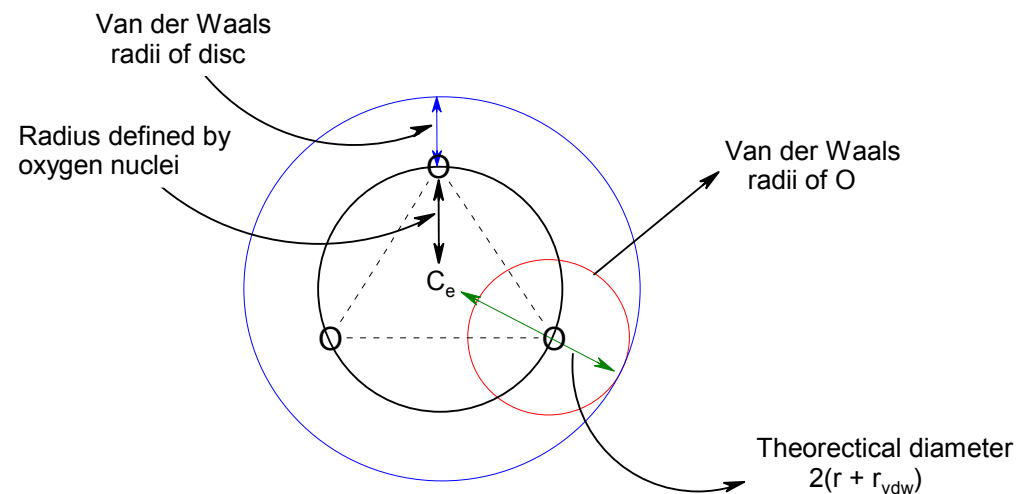
**Figure A** Schematic representation of the arrangement of hexagonal close packed  $\text{PO}_3^{2-}$  or  $\text{PO}_3\text{H}^-$  units. In practice the radius of the packed disc will depend on the van der Waals radii of anionic and protonated O-atoms.

The radius of this disc ( $r$  in **a**, Figure B) can be calculated using trigonometry. The length of a P-O bond can be taken to be  $1.57 \text{ \AA}$ .<sup>1,2</sup> Using the *sine* rule, the O·····O distance (see **b** in Figure B) is  $2(1.57 \sin 109.5^\circ/2) = 2.56 \text{ \AA}$ .



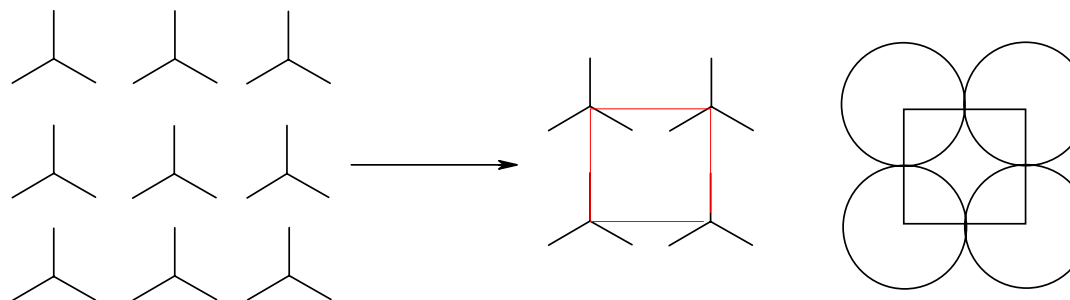
**Figure B** Using trigonometry to calculate the radius of a disc ( $C_e$  is the centroid).

The radius defined by the nuclei of the oxygen atoms ( $c$  in Figure B) is  $(2.56/2)/\sin 60^\circ = 1.48 \text{ \AA}$ . The diameter of the  $\text{PO}_3^{2-}$  disc is defined as twice the distance from the centroid ( $C_e$ ) to the nucleus of an O atom, *plus* the van der Waals radius of oxygen,  $1.40 \text{ \AA}$ ,<sup>3</sup> see Figure C, i.e.  $2(r + r_{\text{vdw}}) = 2(1.48 + 1.40) = 5.76 \text{ \AA}$ .



**Figure C** Schematic representation of the radius of a  $\text{PO}_3^{2-}$  disc.

For primitive packing of  $\text{PO}_3^{2-}$  as in Figure D, the area of the surface required per molecule is equal to the diameter of the disc squared, because each square shown contains four quarters of a molecule. Hence the area required per molecule is  $5.76^2 = 33.2 \text{ \AA}^2$ .



**Figure D** Schematic illustration of the arrangement of primitive close packing.

For hexagonal close-packing (Figure A), the surface area required per molecule is equal to twice the area of the equilateral triangle shown [ $(\frac{1}{2} \times \text{base}) \times \text{height}$ ], because each triangle contains  $3 \times \frac{1}{6}$  of a molecule. Hence the surface area required per molecule is  $2[(\frac{1}{2} \times 5.76) \times (5.76 \sin 60^\circ)] = 28.7 \text{ \AA}^2$ .

These theoretical areas can be compared with those determined experimentally by adsorption isotherms. The specific surface area for the ATH was determined by BET methods<sup>4</sup> to be  $6.0 \text{ m}^2 \text{ g}^{-1}$ . If the isotherm for **9** (without pH adjustment prior to analysis, *ca.* pH 3.0) is fitted by the Langmuir equation, the uptake is  $20.0 (\pm 0.4) \times 10^{-6} \text{ mol g}^{-1}$ .

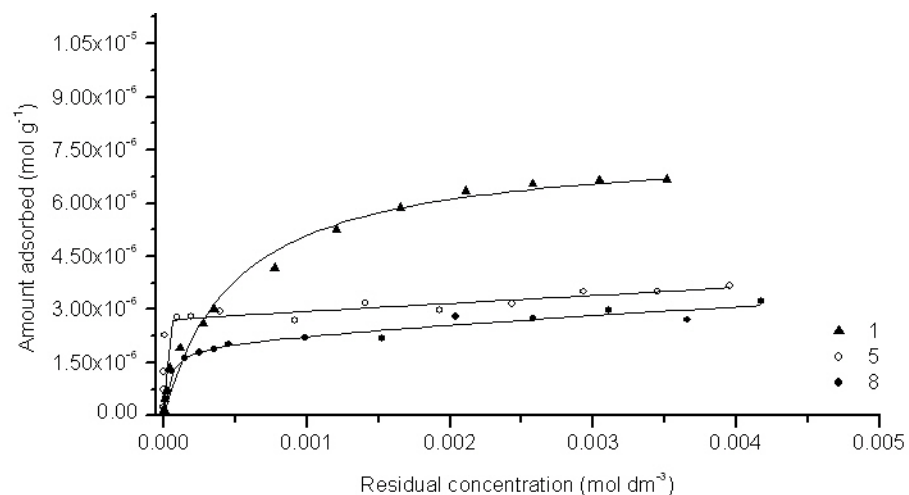
As one gram of ATH has a surface area of  $6.0 \text{ m}^2$  the saturation surface coverage =  $20.0 (\pm 0.4) \times 10^{-6} / 6.0 = 3.33 (\pm 0.07) \times 10^{-6} \text{ g m}^2$ . Multiplication by Avogadro's number gives  $3.33 (\pm 0.07) \times (6.02 \times 10^{17}) = 20.1 (\pm 0.4) \times 10^{17} \text{ molecules m}^{-2}$  or  $20.1 (\pm 0.4) \times 10^{17} / 10^{20} = 20.1 (\pm 0.4) \times 10^{-3} \text{ molecules \AA}^{-2}$ . Thus the area occupied by a single molecule =  $1 / 20.1 (\pm 0.4) \times 10^{-3} = 48 (\pm 5) \text{ \AA}^2$ .

For the isotherm determined with solutions made up to pH 8.5, the observed surface coverage is significantly smaller,  $5.1 (\pm 0.3) \times 10^{-6} \text{ mol g}^{-1}$  (Table 3), and consequently the apparent area per adsorbed molecule is larger,  $195 (\pm 9) \text{ \AA}^2$ .

For 'primitive packing', the surface occupancy is defined by the area of the square shown in Figure D, the sides of which are  $2 \times$  radius of the touching discs. Consequently, the diameter of the discs is  $\sqrt{48} (\pm 5) = 6.9 (\pm 0.4) \text{ \AA}$  for uptake at pH 3.0 and  $14.0 (\pm 0.4) \text{ \AA}$  at pH 8.5. For hexagonal close packing of the disc-shaped head groups (see Figure A), on average a molecule requires twice the area of the triangle shown.

Thus, for saturation at pH 3.0 the area of the triangle =  $48 (\pm 5) / 2 = 24 (\pm 2.5) \text{ \AA}^2$ . As the area of the triangle =  $\frac{1}{2} \times \text{base} \times \text{height} = \frac{1}{2} \times 2r \times 2r \sin 60^\circ = 1.73 r^2$ ,  $r = \sqrt{[24 (\pm 2.5)/1.73]} = 2.83 (\pm 0.2)$  and the diameter =  $7.4 (\pm 0.4) \text{ \AA}$ . For the uptake at pH 8.5 the diameter of the disc representing the head group is  $15.0 (\pm 0.4) \text{ \AA}$ .

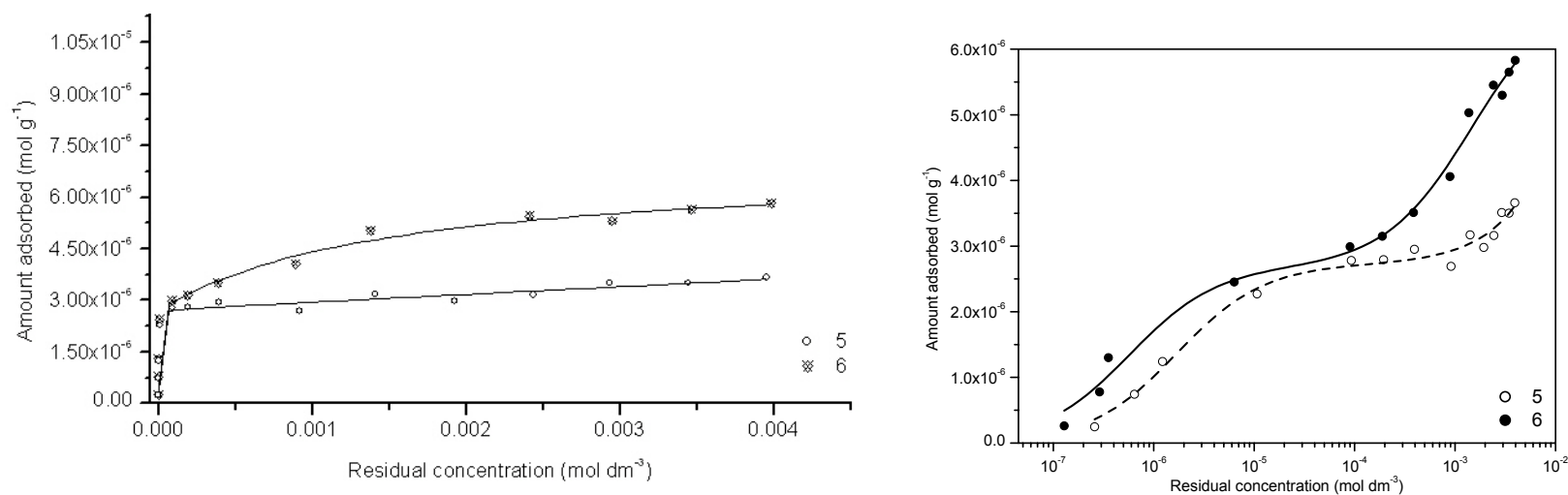
Data for Figure 6 – isotherms of **1**, **5** and **8** (pH 8.5, 25 °C)



| Compound <b>1</b>      |                 | Compound <b>5</b>      |                 | Compound <b>8</b>      |                 |
|------------------------|-----------------|------------------------|-----------------|------------------------|-----------------|
| Residual concentration | Amount adsorbed | Residual concentration | Amount adsorbed | Residual concentration | Amount adsorbed |

| (mol dm <sup>-3</sup> ) | (mol g <sup>-1</sup> ) | (mol dm <sup>-3</sup> ) | (mol g <sup>-1</sup> ) | (mol dm <sup>-3</sup> ) | (mol g <sup>-1</sup> ) |
|-------------------------|------------------------|-------------------------|------------------------|-------------------------|------------------------|
| 3.03E-06                | 1.61E-07               | 2.58E-07                | 2.46E-07               | 4.10E-06                | 1.63E-07               |
| 9.16E-06                | 4.76E-07               | 6.45E-07                | 7.42E-07               | 1.27E-05                | 4.85E-07               |
| 1.86E-05                | 7.12E-07               | 1.23E-06                | 1.24E-06               | 2.55E-05                | 6.98E-07               |
| 4.09E-05                | 1.34E-06               | 1.07E-05                | 2.27E-06               | 5.67E-05                | 1.25E-06               |
| 1.12E-04                | 1.91E-06               | 9.31E-05                | 2.78E-06               | 1.50E-04                | 1.63E-06               |
| 2.74E-04                | 2.60E-06               | 1.94E-04                | 2.79E-06               | 2.51E-04                | 1.80E-06               |
| 3.52E-04                | 3.01E-06               | 3.94E-04                | 2.95E-06               | 3.54E-04                | 1.88E-06               |
| 7.77E-04                | 4.16E-06               | 9.17E-04                | 2.69E-06               | 4.56E-04                | 2.02E-06               |
| 1.21E-03                | 5.27E-06               | 1.41E-03                | 3.17E-06               | 9.87E-04                | 2.19E-06               |
| 1.66E-03                | 5.88E-06               | 1.93E-03                | 2.98E-06               | 1.52E-03                | 2.17E-06               |
| 2.11E-03                | 6.34E-06               | 2.44E-03                | 3.16E-06               | 2.04E-03                | 2.80E-06               |
| 2.58E-03                | 6.54E-06               | 2.93E-03                | 3.51E-06               | 2.58E-03                | 2.74E-06               |
| 3.05E-03                | 6.64E-06               | 3.45E-03                | 3.50E-06               | 3.11E-03                | 2.97E-06               |
| 3.52E-03                | 6.66E-06               | 3.95E-03                | 3.66E-06               | 3.66E-03                | 2.70E-06               |
| -                       | -                      | -                       | -                      | 4.18E-03                | 3.24E-06               |

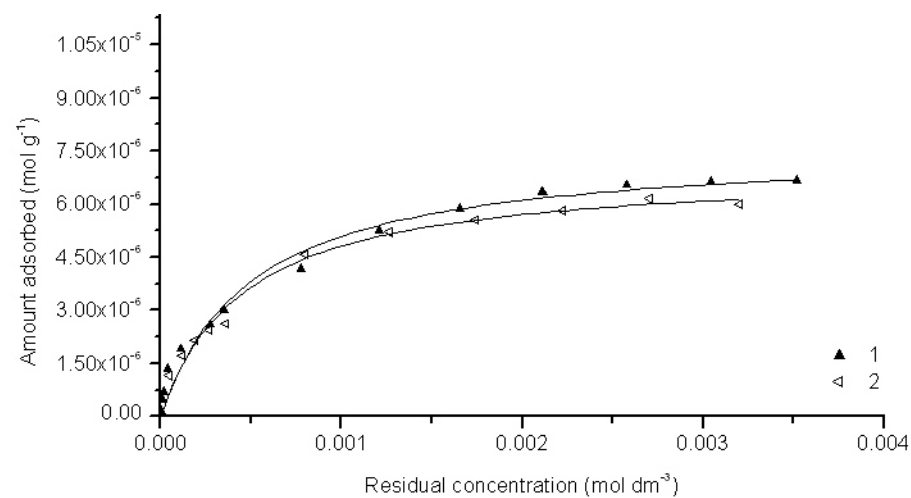
Data for Figure 7 – isotherms of **5** and **6** (right graph plotted on a logarithmic scale), pH 8.5, 25 °C



|                   |                   |
|-------------------|-------------------|
| Compound <b>5</b> | Compound <b>6</b> |
|-------------------|-------------------|

| Residual concentration<br>(mol dm <sup>-3</sup> ) | Amount adsorbed<br>(mol g <sup>-1</sup> ) | Residual concentration<br>(mol dm <sup>-3</sup> ) | Amount adsorbed<br>(mol g <sup>-1</sup> ) |
|---------------------------------------------------|-------------------------------------------|---------------------------------------------------|-------------------------------------------|
| 2.58E-07                                          | 2.46E-07                                  | 1.29E-07                                          | 2.60E-07                                  |
| 6.45E-07                                          | 7.42E-07                                  | 2.90E-07                                          | 7.77E-07                                  |
| 1.23E-06                                          | 1.24E-06                                  | 3.55E-07                                          | 1.30E-06                                  |
| 1.07E-05                                          | 2.27E-06                                  | 6.36E-06                                          | 2.45E-06                                  |
| 9.31E-05                                          | 2.78E-06                                  | 9.01E-05                                          | 2.99E-06                                  |
| 1.94E-04                                          | 2.79E-06                                  | 1.89E-04                                          | 3.15E-06                                  |
| 3.94E-04                                          | 2.95E-06                                  | 3.86E-04                                          | 3.51E-06                                  |
| 9.17E-04                                          | 2.69E-06                                  | 8.91E-04                                          | 4.06E-06                                  |
| 1.41E-03                                          | 3.17E-06                                  | 1.38E-03                                          | 5.03E-06                                  |
| 1.93E-03                                          | 2.98E-06                                  | 2.41E-03                                          | 5.45E-06                                  |
| 2.44E-03                                          | 3.16E-06                                  | 2.95E-03                                          | 5.30E-06                                  |
| 2.93E-03                                          | 3.51E-06                                  | 3.46E-03                                          | 5.65E-06                                  |
| 3.45E-03                                          | 3.50E-06                                  | 3.98E-03                                          | 5.83E-06                                  |
| 3.95E-03                                          | 3.66E-06                                  | -                                                 | -                                         |

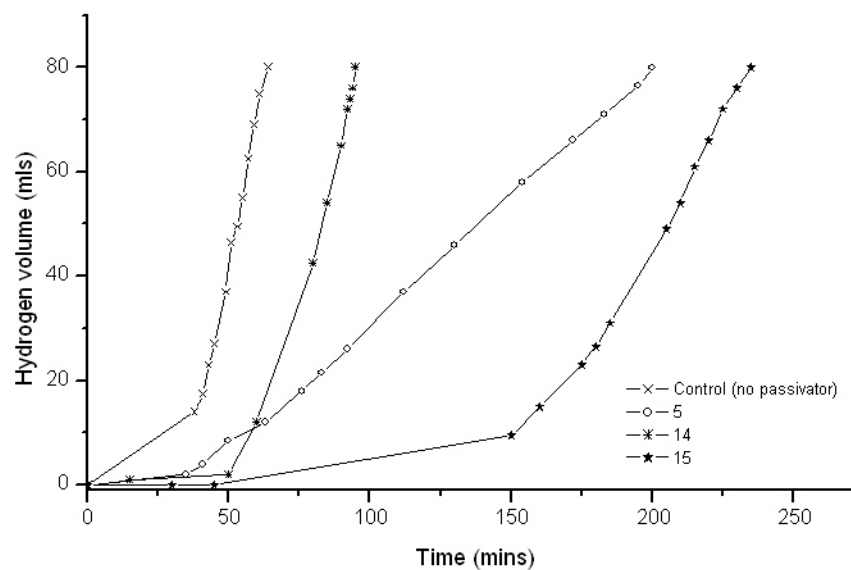
*Data for isotherms of compounds 1 and 2 (pH 8.5, 25 °C)*



|            |            |
|------------|------------|
| Compound 1 | Compound 2 |
|------------|------------|

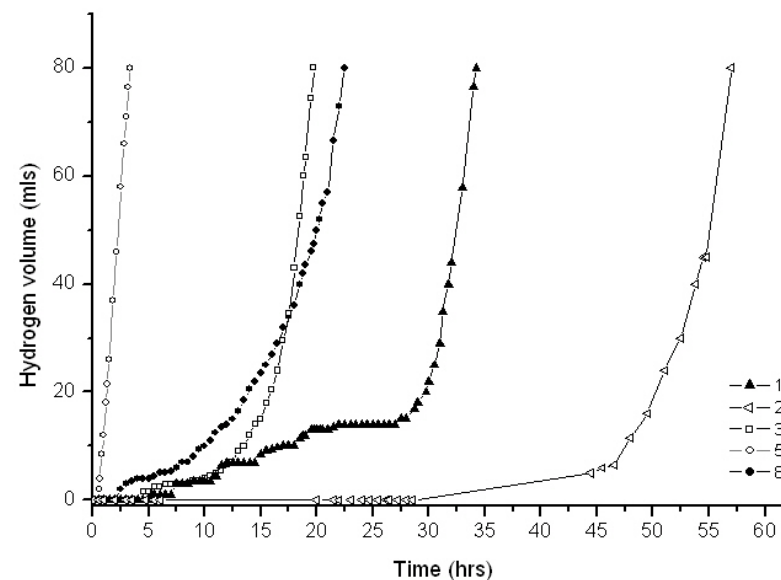
| Residual concentration (mol dm <sup>-3</sup> ) | Amount adsorbed (mol g <sup>-1</sup> ) | Residual concentration (mol dm <sup>-3</sup> ) | Amount adsorbed (mol g <sup>-1</sup> ) |
|------------------------------------------------|----------------------------------------|------------------------------------------------|----------------------------------------|
| 3.03E-06                                       | 1.61E-07                               | 4.57E-05                                       | 1.16E-06                               |
| 9.16E-06                                       | 4.76E-07                               | 1.15E-04                                       | 1.72E-06                               |
| 1.86E-05                                       | 7.12E-07                               | 1.80E-04                                       | 2.14E-06                               |
| 4.09E-05                                       | 1.34E-06                               | 2.70E-04                                       | 2.45E-06                               |
| 1.12E-04                                       | 1.91E-06                               | 3.57E-04                                       | 2.62E-06                               |
| 2.74E-04                                       | 2.60E-06                               | 7.99E-04                                       | 4.57E-06                               |
| 3.52E-04                                       | 3.01E-06                               | 1.27E-03                                       | 5.20E-06                               |
| 7.77E-04                                       | 4.16E-06                               | 1.74E-03                                       | 5.55E-06                               |
| 1.21E-03                                       | 5.27E-06                               | 2.22E-03                                       | 5.82E-06                               |
| 1.66E-03                                       | 5.88E-06                               | 2.70E-03                                       | 6.15E-06                               |
| 2.11E-03                                       | 6.34E-06                               | 3.20E-03                                       | 5.99E-06                               |
| 2.58E-03                                       | 6.54E-06                               | -                                              | -                                      |
| 3.05E-03                                       | 6.64E-06                               | -                                              | -                                      |
| 3.52E-03                                       | 6.66E-06                               | -                                              | -                                      |

Data for Figure 8 – hydrogen evolution test results for the control, 5, 14 and 15 (pH 8, 52 °C)



| Control (no passivator) |                      | Compound <b>5</b> |                      | Compound <b>14</b> |                      | Compound <b>15</b> |                      |
|-------------------------|----------------------|-------------------|----------------------|--------------------|----------------------|--------------------|----------------------|
| Time (mins)             | Hydrogen volume (ml) | Time (mins)       | Hydrogen volume (ml) | Time (mins)        | Hydrogen volume (ml) | Time (mins)        | Hydrogen volume (ml) |
| 0                       | 0                    | 0                 | 0                    | 0                  | 0                    | 0                  | 0                    |
| 38                      | 14                   | 35                | 2                    | 15                 | 1                    | 30                 | 0                    |
| 41                      | 17.5                 | 41                | 4                    | 50                 | 2                    | 45                 | 0                    |
| 43                      | 23                   | 50                | 8.5                  | 60                 | 12                   | 150                | 9.5                  |
| 45                      | 27                   | 63                | 12                   | 80                 | 42.5                 | 160                | 15                   |
| 49                      | 37                   | 76                | 18                   | 85                 | 54                   | 175                | 23                   |
| 51                      | 46.5                 | 83                | 21.5                 | 90                 | 65                   | 180                | 26.5                 |
| 53                      | 49.5                 | 92                | 26                   | 92                 | 72                   | 185                | 31                   |
| 55                      | 55                   | 112               | 37                   | 93                 | 74                   | 205                | 49                   |
| 57                      | 62.5                 | 130               | 46                   | 94                 | 76                   | 210                | 54                   |
| 59                      | 69                   | 154               | 58                   | 95                 | 80                   | 215                | 61                   |
| 61                      | 75                   | 172               | 66                   | -                  | -                    | 220                | 66                   |
| 64                      | 80                   | 183               | 71                   | -                  | -                    | 225                | 72                   |
| -                       | -                    | 195               | 76.5                 | -                  | -                    | 230                | 76                   |
| -                       | -                    | 200               | 80                   | -                  | -                    | 235                | 80                   |

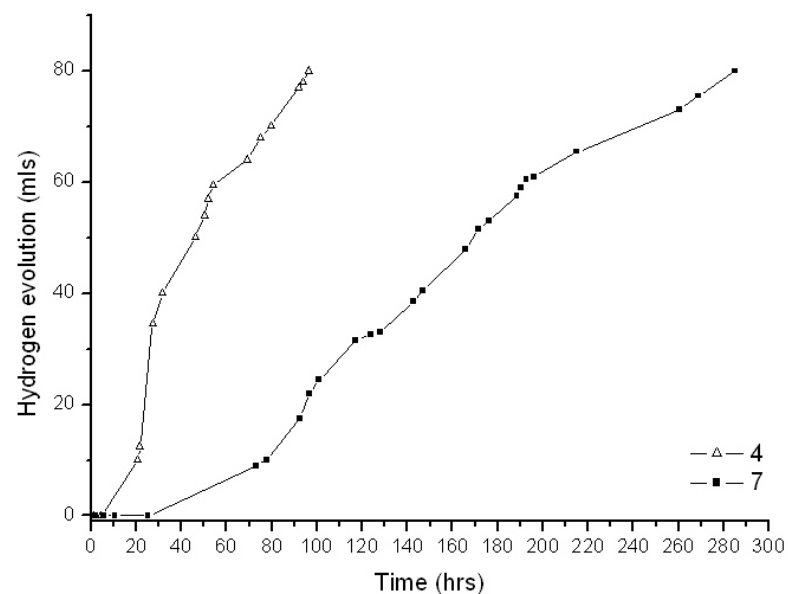
*Data for Figure 9 – hydrogen evolution test results for 1, 2, 3, 5 and 8 (pH 8, 52 °C)*



| Compound 1  |                            |             |                            | Compound 2  |                            | Compound 3  |                            | Compound 5  |                            | Compound 8  |                            |
|-------------|----------------------------|-------------|----------------------------|-------------|----------------------------|-------------|----------------------------|-------------|----------------------------|-------------|----------------------------|
| Time (mins) | H <sub>2</sub> volume (ml) | Time (mins) | H <sub>2</sub> volume (ml) | Time (mins) | H <sub>2</sub> volume (ml) | Time (mins) | H <sub>2</sub> volume (ml) | Time (mins) | H <sub>2</sub> volume (ml) | Time (mins) | H <sub>2</sub> volume (ml) |
| 0           | 0                          | 22.5        | 14                         | 0           | 0                          | 0           | 0                          | 0           | 0                          | 0           | 0                          |
| 0.5         | 0                          | 23          | 14                         | 0.5         | 0                          | 0.5         | 0                          | 0.58        | 2                          | 0.5         | 0                          |
| 1           | 0                          | 23.5        | 14                         | 1           | 0                          | 1           | 0                          | 0.66        | 4                          | 1           | 0                          |
| 1.5         | 0                          | 24          | 14                         | 2           | 0                          | 1.5         | 0                          | 0.83        | 8.5                        | 1.5         | 0                          |
| 2           | 0                          | 24.5        | 14                         | 3           | 0                          | 2           | 0                          | 1           | 12                         | 2           | 0                          |
| 2.5         | 0                          | 25          | 14                         | 3.5         | 0                          | 2.5         | 0                          | 1.2         | 18                         | 2.5         | 2                          |
| 3           | 0                          | 25.5        | 14                         | 4.75        | 0                          | 3           | 0                          | 1.33        | 21.5                       | 3           | 3                          |
| 3.5         | 0                          | 26          | 14                         | 5.5         | 0                          | 3.5         | 0                          | 1.5         | 26                         | 3.5         | 3.5                        |
| 4           | 0                          | 26.5        | 14                         | 6           | 0                          | 4           | 0                          | 1.83        | 37                         | 4           | 4                          |
| 4.5         | 0                          | 27          | 14                         | 20          | 0                          | 4.5         | 1.5                        | 2.16        | 46                         | 4.5         | 4                          |
| 5           | 0                          | 27.5        | 15                         | 21.5        | 0                          | 5           | 1.5                        | 2.5         | 58                         | 5           | 4                          |
| 5.25        | 1                          | 28          | 15                         | 22          | 0                          | 5.5         | 2.5                        | 2.83        | 66                         | 5.5         | 4.5                        |
| 5.5         | 1                          | 28.75       | 17                         | 23          | 0                          | 6           | 2.5                        | 3           | 71                         | 6           | 5                          |
| 6           | 1                          | 29          | 18                         | 24          | 0                          | 6.5         | 3                          | 3.2         | 76.5                       | 6.5         | 5                          |
| 6.5         | 1                          | 29.75       | 20                         | 24.75       | 0                          | 7           | 3                          | 3.35        | 80                         | 7           | 5.25                       |
| Compound 1  |                            |             |                            | Compound 2  |                            | Compound 3  |                            | Compound 5  |                            | Compound 8  |                            |

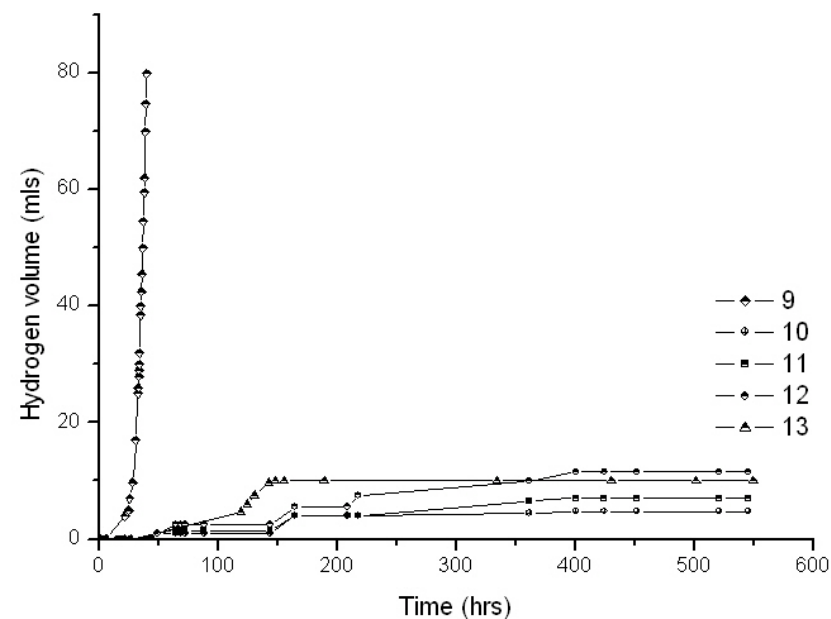
| Time (mins) | H <sub>2</sub> volume (ml) | Time (mins) | H <sub>2</sub> volume (ml) | Time (mins) | H <sub>2</sub> volume (ml) | Time (mins) | H <sub>2</sub> volume (ml) | Time (mins) | H <sub>2</sub> volume (ml) | Time (mins) | H <sub>2</sub> volume (ml) |
|-------------|----------------------------|-------------|----------------------------|-------------|----------------------------|-------------|----------------------------|-------------|----------------------------|-------------|----------------------------|
| 7           | 1                          | 30          | 22                         | 25.5        | 0                          | 7.5         | 3                          | -           | -                          | 7.5         | 6                          |
| 7.5         | 3                          | 30.5        | 25                         | 26.25       | 0                          | 8           | 3                          | -           | -                          | 8           | 7                          |
| 8           | 3                          | 31          | 29                         | 26.5        | 0                          | 8.5         | 3                          | -           | -                          | 8.5         | 7                          |
| 8.5         | 3                          | 31.25       | 35                         | 27.25       | 0                          | 9           | 3.5                        | -           | -                          | 9           | 8                          |
| 9           | 3.5                        | 31.75       | 40                         | 28          | 0                          | 9.5         | 3.5                        | -           | -                          | 9.5         | 9.5                        |
| 9.5         | 3.5                        | 32          | 44                         | 28.5        | 0                          | 10          | 4                          | -           | -                          | 10          | 10                         |
| 10          | 3.5                        | 33          | 58                         | 44.5        | 5                          | 10.5        | 4.5                        | -           | -                          | 10.5        | 11                         |
| 10.5        | 3.5                        | 34          | 76.5                       | 45.5        | 6                          | 11          | 5                          | -           | -                          | 11          | 12.5                       |
| 11          | 4.5                        | 34.25       | 80                         | 46.5        | 6.5                        | 11.5        | 5.5                        | -           | -                          | 11.5        | 13.5                       |
| 11.5        | 6.5                        | -           | -                          | 48          | 11.5                       | 12          | 6.5                        | -           | -                          | 12          | 14                         |
| 12          | 7                          | -           | -                          | 49.5        | 16                         | 12.5        | 7                          | -           | -                          | 12.5        | 15                         |
| 12.5        | 7                          | -           | -                          | 51          | 24                         | 13          | 9                          | -           | -                          | 13          | 16.5                       |
| 13          | 7                          | -           | -                          | 52.5        | 30                         | 13.5        | 10                         | -           | -                          | 13.5        | 18.5                       |
| 13.5        | 7                          | -           | -                          | 53.75       | 40                         | 14          | 12                         | -           | -                          | 14          | 20.5                       |
| 14          | 7                          | -           | -                          | 54.5        | 45                         | 14.5        | 14                         | -           | -                          | 14.5        | 22                         |
| 14.5        | 7                          | -           | -                          | 54.75       | 45                         | 15          | 15                         | -           | -                          | 15          | 23.5                       |
| 15          | 8.5                        | -           | -                          | 57          | 80                         | 15.5        | 18                         | -           | -                          | 15.5        | 25                         |
| 15.5        | 9.25                       | -           | -                          | -           | -                          | 16          | 20.5                       | -           | -                          | 16          | 27                         |
| 16          | 9.5                        | -           | -                          | -           | -                          | 16.5        | 24                         | -           | -                          | 16.5        | 29                         |
| 16.5        | 9.75                       | -           | -                          | -           | -                          | 17          | 29.5                       | -           | -                          | 17          | 32                         |
| 17          | 10                         | -           | -                          | -           | -                          | 17.5        | 34.5                       | -           | -                          | 17.5        | 34                         |
| 17.5        | 10                         | -           | -                          | -           | -                          | 18          | 43                         | -           | -                          | 18          | 36                         |
| 18          | 10                         | -           | -                          | -           | -                          | 18.5        | 52.5                       | -           | -                          | 18.5        | 40                         |
| 18.5        | 11.5                       | -           | -                          | -           | -                          | 18.8        | 60                         | -           | -                          | 18.8        | 42                         |
| 18.8        | 12                         | -           | -                          | -           | -                          | 19          | 63.5                       | -           | -                          | 19          | 43.5                       |
| 19          | 12                         | -           | -                          | -           | -                          | 19.5        | 74.5                       | -           | -                          | 19.5        | 46                         |
| 19.5        | 13                         | -           | -                          | -           | -                          | 19.75       | 80                         | -           | -                          | 19.75       | 47.5                       |
| 19.75       | 13                         | -           | -                          | -           | -                          | -           | -                          | -           | -                          | 20          | 50                         |
| 20          | 13                         | -           | -                          | -           | -                          | -           | -                          | -           | -                          | 20.25       | 52                         |
| 20.25       | 13                         | -           | -                          | -           | -                          | -           | -                          | -           | -                          | 20.5        | 55                         |
| 20.5        | 13                         | -           | -                          | -           | -                          | -           | -                          | -           | -                          | 21          | 57                         |
| 21          | 13                         | -           | -                          | -           | -                          | -           | -                          | -           | -                          | 21.5        | 66.5                       |
| 21.5        | 13.5                       | -           | -                          | -           | -                          | -           | -                          | -           | -                          | 22          | 73                         |
| 22          | 14                         | -           | -                          | -           | -                          | -           | -                          | -           | -                          | 22.5        | 80                         |

*Data for Figure 11 – hydrogen evolution test results for 4 and 7 (pH 8, 52 °C)*



| Compound 4  |                      |             |                      | Compound 7  |                      |             |                      |
|-------------|----------------------|-------------|----------------------|-------------|----------------------|-------------|----------------------|
| Time (mins) | Hydrogen volume (ml) | Time (mins) | Hydrogen volume (ml) | Time (mins) | Hydrogen volume (ml) | Time (mins) | Hydrogen volume (ml) |
| 0           | 0                    | 94          | 78                   | 0           | 0                    | 142.5       | 38.5                 |
| 1.25        | 0                    | 96.25       | 80                   | 1           | 0                    | 147         | 40.5                 |
| 4.5         | 0                    | -           | -                    | 1.5         | 0                    | 165.75      | 48                   |
| 20.75       | 10                   | -           | -                    | 2           | 0                    | 171.5       | 51.5                 |
| 21.75       | 12.5                 | -           | -                    | 5.5         | 0                    | 176         | 53                   |
| 27.25       | 34.5                 | -           | -                    | 10.5        | 0                    | 188.5       | 57.5                 |
| 31.5        | 40                   | -           | -                    | 25.25       | 0                    | 190.5       | 59                   |
| 46          | 50                   | -           | -                    | 73          | 9                    | 192.75      | 60.5                 |
| 50.5        | 54                   | -           | -                    | 77.75       | 10                   | 196.25      | 61                   |
| 52          | 57                   | -           | -                    | 92.5        | 17.5                 | 215         | 65.5                 |
| 54          | 59.5                 | -           | -                    | 96.75       | 22                   | 260.5       | 73                   |
| 69.25       | 64                   | -           | -                    | 101         | 24.5                 | 268.75      | 75.5                 |
| 75          | 68                   | -           | -                    | 117.25      | 31.5                 | 285         | 80                   |
| 79.5        | 70                   | -           | -                    | 123.75      | 32.5                 | -           | -                    |
| 92          | 77                   | -           | -                    | 128         | 33                   | -           | -                    |

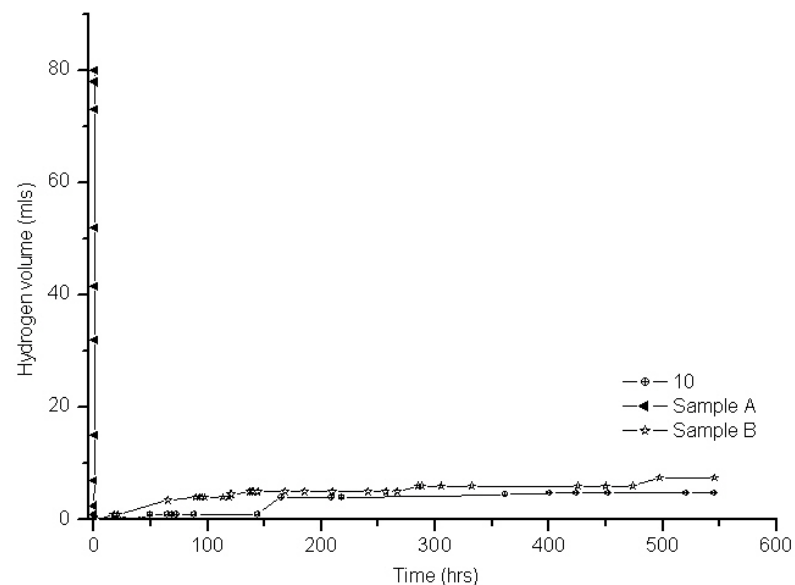
Data for Figure 12 – hydrogen evolution test results for **9**, **10**, **11**, **12** and **13** (pH 8, 52 °C)



| Compound 9  |                      | Compound 10 |                      | Compound 11 |                      | Compound 12 |                      | Compound 13 |                      |
|-------------|----------------------|-------------|----------------------|-------------|----------------------|-------------|----------------------|-------------|----------------------|
| Time (mins) | Hydrogen volume (ml) | Time (mins) | Hydrogen volume (ml) | Time (mins) | Hydrogen volume (ml) | Time (mins) | Hydrogen volume (ml) | Time (mins) | Hydrogen volume (ml) |
| 0           | 0                    | 0           | 0                    | 0           | 0                    | 0           | 0                    | 0           | 0                    |
| 1           | 0                    | 0.5         | 0                    | 0.5         | 0                    | 0.5         | 0                    | 1.25        | 0                    |
| 6.5         | 0                    | 1           | 0                    | 1           | 0                    | 1           | 0                    | 2           | 0                    |
| 22          | 4                    | 1.5         | 0                    | 1.5         | 0                    | 1.5         | 0                    | 5.5         | 0                    |
| 24          | 4.75                 | 2           | 0                    | 2           | 0                    | 2           | 0                    | 7           | 0                    |
| 25          | 5                    | 16.75       | 0                    | 16.75       | 0                    | 16.75       | 0                    | 21.5        | 0                    |
| 26          | 7                    | 18.5        | 0                    | 18.5        | 0                    | 18.5        | 0                    | 27.5        | 0                    |
| 28.5        | 9.75                 | 21.5        | 0                    | 21.5        | 0                    | 21.5        | 0                    | 119.5       | 4.75                 |
| 31.25       | 17                   | 27          | 0                    | 27          | 0                    | 27          | 0                    | 125         | 6                    |
| 33          | 25                   | 40.75       | 0                    | 40.75       | 0                    | 40.75       | 0                    | 131         | 7.5                  |
| 33.25       | 26                   | 44.5        | 0                    | 44.5        | 0                    | 44.5        | 0                    | 143         | 9.75                 |
| 33.5        | 28                   | 49.5        | 1                    | 49.5        | 1                    | 49.5        | 1                    | 148.5       | 10                   |
| 33.75       | 29                   | 64.75       | 1                    | 64.75       | 1.5                  | 64.75       | 2.5                  | 156         | 10                   |

|                    |                             |                    |                             |                    |                             |                    |                             |                    |                             |
|--------------------|-----------------------------|--------------------|-----------------------------|--------------------|-----------------------------|--------------------|-----------------------------|--------------------|-----------------------------|
| 34                 | 30                          | 69                 | 1                           | 69                 | 1.5                         | 69                 | 2.5                         | 189.5              | 10                          |
| Compound 9         |                             | Compound 10        |                             | Compound 11        |                             | Compound 12        |                             | Compound 13        |                             |
| <b>Time (mins)</b> | <b>Hydrogen volume (ml)</b> | <b>Time (mins)</b> | <b>Hydrogen volume (ml)</b> | <b>Time (mins)</b> | <b>Hydrogen volume (ml)</b> | <b>Time (mins)</b> | <b>Hydrogen volume (ml)</b> | <b>Time (mins)</b> | <b>Hydrogen volume (ml)</b> |
| 34.25              | 32                          | 72.5               | 1                           | 72.5               | 1.5                         | 72.5               | 2.5                         | 334.5              | 10                          |
| 35.25              | 38.5                        | 88.5               | 1                           | 88.5               | 1.5                         | 88.5               | 2.5                         | 430.5              | 10                          |
| 35.5               | 40                          | 144                | 1                           | 144                | 1.5                         | 144                | 2.5                         | 501.5              | 10                          |
| 35.75              | 42.5                        | 164.75             | 4                           | 164.75             | 4                           | 164.75             | 5.5                         | 549.5              | 10                          |
| 36.5               | 45.5                        | 209                | 4                           | 209                | 4                           | 209                | 5.5                         | -                  | -                           |
| 37                 | 50                          | 217.75             | 4                           | 217.75             | 4                           | 217.75             | 7.5                         | -                  | -                           |
| 37.5               | 54.5                        | 361.5              | 4.5                         | 361.5              | 6.5                         | 361.5              | 10                          | -                  | -                           |
| 38.25              | 59.5                        | 400.5              | 4.75                        | 400.5              | 7                           | 400.5              | 11.5                        | -                  | -                           |
| 38.5               | 62                          | 424.5              | 4.75                        | 424.5              | 7                           | 424.5              | 11.5                        | -                  | -                           |
| 39                 | 70                          | 452                | 4.75                        | 452                | 7                           | 452                | 11.5                        | -                  | -                           |
| 39.5               | 74.75                       | 521                | 4.75                        | 521                | 7                           | 521                | 11.5                        | -                  | -                           |
| 40                 | 80                          | 545.5              | 4.75                        | 545.5              | 7                           | 545.5              | 11.5                        | -                  | -                           |

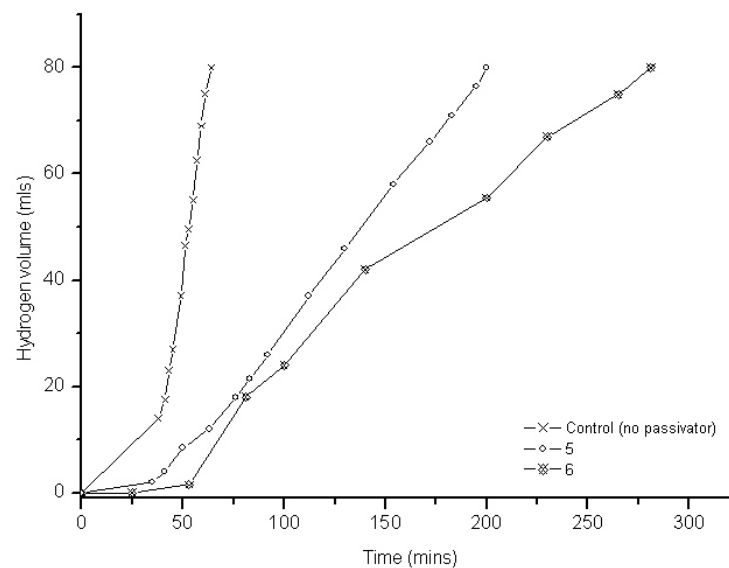
Data for Figure 13 – hydrogen evolution test results for **10** and commercial samples **A** and **B** (pH 8, 52 °C)



| Compound <b>10</b> |                      | Sample <b>A</b> |                      | Sample <b>B</b> |                      |
|--------------------|----------------------|-----------------|----------------------|-----------------|----------------------|
| Time (mins)        | Hydrogen volume (ml) | Time (mins)     | Hydrogen volume (ml) | Time (mins)     | Hydrogen volume (ml) |
| 0                  | 0                    | 0               | 0                    | 0               | 0                    |
| 0.5                | 0                    | 0.25            | 0                    | 0.25            | 0                    |
| 1                  | 0                    | 0.267           | 1                    | 1               | 0                    |
| 1.5                | 0                    | 0.33            | 2.5                  | 1.75            | 0                    |
| 2                  | 0                    | 0.42            | 7                    | 2.25            | 0                    |
| 16.75              | 0                    | 0.5             | 15                   | 3.25            | 0                    |
| 18.5               | 0                    | 0.633           | 32                   | 17.5            | 1                    |
| 21.5               | 0                    | 0.667           | 41.5                 | 18.5            | 1                    |
| 27                 | 0                    | 0.75            | 52                   | 21              | 1                    |
| 40.75              | 0                    | 0.83            | 73                   | 65.5            | 3.5                  |
| 44.5               | 0                    | 0.85            | 78                   | 89.5            | 4                    |
| 49.5               | 1                    | 0.858           | 80                   | 93              | 4                    |
| 64.75              | 1                    | -               | -                    | 94.75           | 4                    |

|             |                         |             |                         |             |                         |
|-------------|-------------------------|-------------|-------------------------|-------------|-------------------------|
| 69          | 1                       | -           | -                       | 97.75       | 4                       |
| 72.5        | 1                       | -           | -                       | 113.75      | 4                       |
| Compound 10 |                         | Sample A    |                         | Sample B    |                         |
| Time (mins) | Hydrogen<br>volume (ml) | Time (mins) | Hydrogen<br>volume (ml) | Time (mins) | Hydrogen<br>volume (ml) |
| 88.5        | 1                       | -           | -                       | 119.25      | 4                       |
| 144         | 1                       | -           | -                       | 120.25      | 4.5                     |
| 164.75      | 4                       | -           | -                       | 120.75      | 4.5                     |
| 209         | 4                       | -           | -                       | 137         | 5                       |
| 217.75      | 4                       | -           | -                       | 139.25      | 5                       |
| 361.5       | 4.5                     | -           | -                       | 140.75      | 5                       |
| 400.5       | 4.75                    | -           | -                       | 144         | 5                       |
| 424.5       | 4.75                    | -           | -                       | 168         | 5                       |
| 452         | 4.75                    | -           | -                       | 185         | 5                       |
| 521         | 4.75                    | -           | -                       | 209.5       | 5                       |
| 545.5       | 4.75                    | -           | -                       | 241         | 5                       |
| -           | -                       | -           | -                       | 256.5       | 5                       |
| -           | -                       | -           | -                       | 266.5       | 5                       |
| -           | -                       | -           | -                       | 285         | 6                       |
| -           | -                       | -           | -                       | 288.25      | 6                       |
| -           | -                       | -           | -                       | 305         | 6                       |
| -           | -                       | -           | -                       | 332         | 6                       |
| -           | -                       | -           | -                       | 425.5       | 6                       |
| -           | -                       | -           | -                       | 449.5       | 6                       |
| -           | -                       | -           | -                       | 473.5       | 6                       |
| -           | -                       | -           | -                       | 497.5       | 7.5                     |
| -           | -                       | -           | -                       | 545.5       | 7.5                     |

*Data for hydrogen evolution test of compound 6 (pH 8, 52 °C)*



| Control (no passivator) |                      | Compound 5  |                      | Compound 6  |                      |
|-------------------------|----------------------|-------------|----------------------|-------------|----------------------|
| Time (mins)             | Hydrogen volume (ml) | Time (mins) | Hydrogen volume (ml) | Time (mins) | Hydrogen volume (ml) |
| 0                       | 0                    | 0           | 0                    | 0           | 0                    |
| 38                      | 14                   | 35          | 2                    | 25          | 0                    |
| 41                      | 17.5                 | 41          | 4                    | 53          | 1.5                  |
| 43                      | 23                   | 50          | 8.5                  | 81          | 18                   |
| 45                      | 27                   | 63          | 12                   | 100         | 24                   |
| 49                      | 37                   | 76          | 18                   | 140         | 42                   |
| 51                      | 46.5                 | 83          | 21.5                 | 200         | 55.5                 |
| 53                      | 49.5                 | 92          | 26                   | 230         | 67                   |
| 55                      | 55                   | 112         | 37                   | 265         | 75                   |
| 57                      | 62.5                 | 130         | 46                   | 281         | 80                   |
| 59                      | 69                   | 154         | 58                   | -           | -                    |

|    |    |     |      |   |   |
|----|----|-----|------|---|---|
| 61 | 75 | 172 | 66   | - | - |
| 64 | 80 | 183 | 71   | - | - |
|    |    | 195 | 76.5 | - | - |
|    |    | 200 | 80   | - | - |

*References*

- <sup>1</sup> F. H. Allen, *Acta Crystallographica, Section B: Structural Science*, 2002, **B58**, 380.
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- <sup>4</sup> P. W. Atkins, '*Physical Chemistry*', Oxford University Press, Oxford, 6th Edition, 1998.