

Newsletter • Autumn 2014

## A SPOTLIGHT ON: IONIC LIQUIDS

Earlier this year we sponsored ILSEPT, a fantastic conference chaired by Dr Mark Shiflett of DuPont and Professor Edward Maginn of the University of Notre Dame in the US. The program focused on the use of ionic liquids (ILs) in separation and purification technology. Our primary US representative John Bullis attended, together with Dr Mark Roper from the UK, and it provided us with an ideal opportunity to showcase our new XEMIS high pressure sorption microbalance.

**"IGA instruments are now firmly established as the tool of choice for this application"**

In recent years, there has been an immense amount of interest in ILs, and their gas and vapor sorption properties have been widely investigated by researchers working in the field. Furthermore, our IGA instruments are now firmly established as the tool of choice for this application<sup>1</sup> and have been widely used for vapor-liquid equilibrium (VLE) studies over the last decade or so.<sup>2-5</sup>



What is less common, however, is the use of our other instruments for the study of these materials.

Our attention was therefore drawn to a recent article by a team of researchers from the Laboratoire Polymères, Biopolymères et Surfaces at the Université de Rouen in France and their collaborators in Algeria and Ukraine.<sup>6</sup> In this study, Professor Stéphane Marais and his co-workers examined the sorption and permeation properties of supported ionic liquid membranes (SILMs) for the separation of water and volatile organic compounds (VOCs).

Supported liquid membranes (SLMs) typically contain organic solvents but this can result in instability due to solvent loss. As an alternative, ILs show great promise for the production of more stable SLMs because of their unique properties, in comparison with other solvents, including their negligible vapor pressure, high chemical and thermal stability, and a high capillary force, which minimizes their removal from the porous membrane support. Of course, for separation applications it is essential to be able to characterize the behavior of a given SILM with respect to the relevant gases and vapors.

The particular SILMs in this study were produced by immobilizing [bmim][BF<sub>4</sub>], [bmim][PF<sub>6</sub>] and [hmim][PF<sub>6</sub>] in

porous membranes prepared from a commercially available polymer, Matrimid 5218.

In contrast to the majority of previous IL studies featuring Hiden Isochema gas and vapor sorption instrumentation, Professor Marais and his co-workers used an IGAsorp. This system operates at ambient pressure in a flowing stream of nitrogen, which is mixed with a wet stream, in varying quantities, to provide precise control of the partial vapor pressure of the active species in the measurement chamber.

In the study, the equilibrium water, ethanol and cyclohexane sorption isotherms were determined for both



the isolated ILs and the host membrane at 25°C. [bmim][BF<sub>4</sub>] was found to absorb the most water and ethanol, and also exhibited the highest selectivities. The membrane containing this ionic liquid was thus selected for further testing.

A moisture vapor transmission rate (MVTR) cell was then used to determine the permeation rates of the three vapors through the selected membrane. The results showed that water had the highest permeability, followed by ethanol and then cyclohexane. They also allowed the calculation of ideal selectivities between each pair of species, which were found to be particularly high for water/cyclohexane and ethanol/cyclohexane.

As well as being a great example of the use of our instruments, we also think this is probably the first example of the use of an IGAsorp to study the sorption of water and hydrocarbon vapors by ILs, but if you know differently, please let us know.

## References

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## 14<sup>th</sup> International Symposium on Metal-Hydrogen Systems: Fundamentals and Applications

In July, over 400 delegates enjoyed unusually warm and sunny weather in Salford and participated in five days of fantastic oral and poster presentations at MH2014.

The technical program featured a number of different sessions within three tracks – Fundamentals, Materials and Applications – covering contributions ranging from the fundamental behavior of hydrogen in binary hydride thin films to the development of practical hydrogen storage units. This packed schedule was supplemented with a varied social program; delegates enjoyed a typically English cream tea at one of three local stately homes and a conference dinner held at Old Trafford, home of Manchester United. The conference proceedings are due to be published soon in a special issue of the *Journal of Alloys and Compounds*.

Hiden Isochema was proud to be a Silver Sponsor of the event and was pleased to be able to provide further organizational support, with Dr Darren Broom being an active member of the local organizing committee. Furthermore, the organizers were delighted with the success of the conference as a whole and have now handed over the baton to Professor Andreas Züttel who will chair the next MH conference in Switzerland in 2016.

An impressive set of photos from the event can be found at: mh2014.salford.ac.uk/photos



Richard Mettaah, Creative Imaging

# MH2014 Summer School a Great Success



The summer school on the characterization of hydrogen-material interactions that we co-hosted with the University of Salford, prior to the main MH2014 conference, was a great success and was attended by 39 students, from institutions in 15 different countries.

Day one of proceedings began with introductory lectures at the University of Salford buildings at MediaCity UK in Manchester, chaired by Dr Martin Owen Jones (ISIS neutron source, UK), one of the event's co-organizers.

The day featured a series of talks covering the behavior of hydrogen in materials. The invited speakers included Professor Andreas Züttel (EPFL and EMPA, Switzerland), Dr Paul Anderson (University of Birmingham, UK), Dr Theodore Steriotis (NCSR "Demokritos", Greece), and Dr Nuno Bimbo (University of Bath, UK).

The second day took place at our headquarters in Warrington. Following a welcome and introduction, Drs Darren Broom and Mark Roper of Hiden Isochema gave



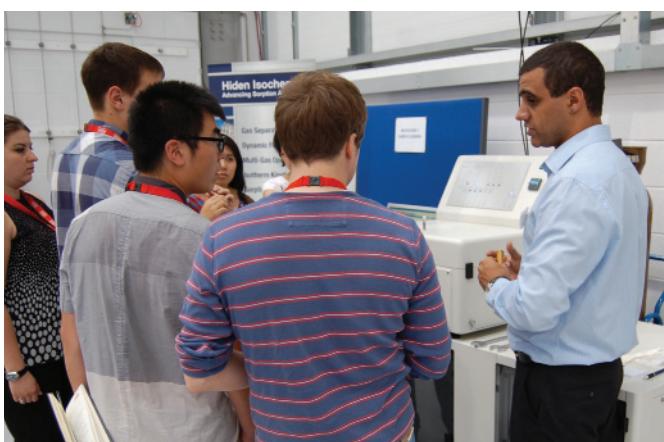
talks entitled "Manometric Measurement of Hydrogen Sorption by Materials" and "Gravimetric Measurement of Hydrogen Sorption by Materials".

These complementary talks addressed the two main macroscopic methods for the determination of hydrogen uptake by materials from a practical perspective and covered many of the issues that can affect these measurements.

The rest of the day was then spent on practical demonstrations of the measurement of hydrogen sorption using a number of different Hiden Isochema instruments. This allowed a further, thorough discussion of the important considerations for the performance of accurate hydrogen sorption measurements.

In addition to the practical demonstrations, the students also visited Hiden Analytical, a well-known manufacturer of quadrupole mass spectrometers and Hiden Isochema's parent company.

Following the intensive day at Hiden, the students were then able to take a break from the scientific program and enjoyed a one day excursion to the picturesque village of



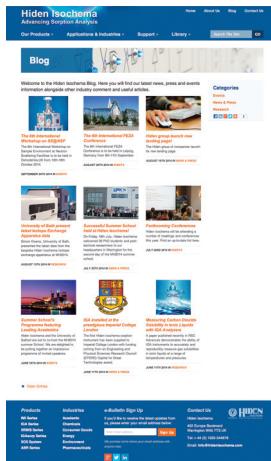


Dr Andreas Borgschulte (EMPA, Switzerland) and Professor Mark Conradi (Washington University, USA).

The feedback that we have received has been very positive. We also hope that the students both enjoyed and benefited from the varied program on offer.

For more details, please see our blog: [isochema.com/summerschool](http://isochema.com/summerschool)

# News From Our Blog



- IGA installed at prestigious Imperial College London
  - University of Bath present latest Isotope Exchange Apparatus data
  - Hiden Group launch new landing page

To find out more about any of these stories, or to read our other blog items, please visit:  
[isochema.com/blog](http://isochema.com/blog)

## **NEW Applications Articles:**

## “Separation of rare gases and chiral molecules by selective binding in porous organic cages” L. Chai, J. J. N. L. M. Mulder, *J. Mater. Chem.*, 12 (2011) 2514–2522

L. Chen et al. Nature Materials 13 (2014) 954-960

An impressive study featuring both a Hiden Isochema automated breakthrough reactor and an IGA to investigate the removal of low concentrations of Kr and Xe from air using the organic cage molecule CC3.

## "Polymeric molecular sieve membranes via *in situ* cross-linking of non-porous polymer membrane templates"

Z.-A. Qiao et al. Nature Communications 5 (2014) 3705

A team from Oak Ridge National Laboratory and the University of Tennessee in the US use an IGA to characterize the equilibrium uptake of  $\text{CO}_2$  and  $\text{N}_2$  by porous hypercrosslinked polymer membranes for gas separation.

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Grasmere in the Lake District, which is famous for being the home (from 1799 to 1808) of William Wordsworth, one of the best known of England's Romantic Poets.

The summer school then returned to MediaCity UK for the final day, which was chaired by Dr Dan Bull (University of Salford, UK), another of the co-organizers. This featured a series of lectures by invited speakers who each specialize in different microscopic characterization techniques, including Inelastic Neutron Scattering (INS), powder diffraction, and Nuclear Magnetic Resonance (NMR), Raman and Infrared (IR) spectroscopies.

The speakers on the Sunday included Dr Sabrina Sartori (University of Oslo/UNIK and IFE, Norway), Dr Timmy Ramirez-Cuesta (Oak Ridge National Laboratory, USA), and Prof. Mark Cawood (Washington University, USA).

**Hiden Isochema**  
Advancing Sorption Analysis™

## A New Commercial Instrument for Gas Sorption Measurements under Extreme Conditions

### Introduction

High pressure adsorption is of significant interest for a range of applications, including the storage of gases such as hydrogen and methane and the separation and purification of gases from mixtures. In addition, it is important to be able to accurately characterize the adsorption behavior of different materials under extreme conditions. The ability to do this accurately and rapidly, in particular, can be challenging [1]. Furthermore, the compatibility of components for use at high pressures and temperatures is required for environmental applications, for example, a is a serious practical issue.

### Experimental Details

The Hiden Isochema K25 instrument has been the proven platform controlled, and sample weight measured, by a novel proprietary feed system. Sensitive measuring components are located in the vacuum chamber, which is maintained at a pressure of  $10^{-6}$  mbar during measurement. The microbalance has a maximum capacity of  $\pm 0.2$  mg, a weighing range of  $0.2 - 200$  mg, a resolution of  $0.2 \mu\text{g}$ , and a maximum sample temperature of  $400^\circ\text{C}$ . The instrument is controlled via a computer, automated with pressure, temperature and weight readings constantly recorded from time 0 to 1 min intervals. The software allows for the generation of a wide range of plots, including those shown in Figure 1, none of which are component specific.

For this work, the sample was placed in the vacuum chamber, weighed, and then left for several hours at an appropriate temperature. The temperature of the sample was held while gas was adsorbed onto the surface. The gas was then desorbed, and the pressure was recorded for desorption, the gas pressure being constantly regulated in all cases using a Hiden Isochema K25 gas delivery system integrated with the K25.

Figure 1 Hiden Isochema schematic.

### Results and Discussion

Figure 2 shows (G) adsorption-desorption isotherms for the carbon nanotube sample. The data were collected at 200, 250, 298, and 300 K. It can be seen that the isotherms are very similar, demonstrating both the excellent long term stability of the K25 and the reliability of the data at these temperatures. The pressure resolution on the kymograph pressure recorder consisted of 0.05 upwards.

Pressure (bar)	200 K (mg/g)	250 K (mg/g)	298 K (mg/g)	300 K (mg/g)
0	0.00	0.00	0.00	0.00
20	0.05	0.05	0.05	0.05
40	0.10	0.10	0.10	0.10
60	0.15	0.15	0.15	0.15
80	0.20	0.20	0.20	0.20
100	0.20	0.20	0.20	0.20
120	0.20	0.20	0.20	0.20
140	0.20	0.20	0.20	0.20
160	0.20	0.20	0.20	0.20
180	0.20	0.20	0.20	0.20
200	0.20	0.20	0.20	0.20

Figure 2 (G) Adsorption-desorption isotherms for a carbon nanotube sample. (Data courtesy of University of Nottingham).

Figure 3 shows (H) adsorption isotherms at an initial pressure of 1 bar for the same sample taken at 12.5, 20, 50, 100, and 150 °C. It can be seen that the isotherms are very similar, demonstrating both the excellent long term stability of the K25 and the reliability of the data at these temperatures.

The pressure resolution on the kymograph pressure recorder consisted of 0.05 upwards. The data were collected at 12.5, 20, 50, 100, and 150 °C, and then the sample was cooled back down to 12.5 °C, and the process repeated. The isotherms are very similar, demonstrating both the excellent long term stability of the K25 and the reliability of the data at these temperatures.

Pressure (bar)	12.5 °C (mg/g)	20 °C (mg/g)	50 °C (mg/g)	100 °C (mg/g)	150 °C (mg/g)
0	0.00	0.00	0.00	0.00	0.00
20	0.05	0.05	0.05	0.05	0.05
40	0.10	0.10	0.10	0.10	0.10
60	0.15	0.15	0.15	0.15	0.15
80	0.20	0.20	0.20	0.20	0.20
100	0.20	0.20	0.20	0.20	0.20
120	0.20	0.20	0.20	0.20	0.20
140	0.20	0.20	0.20	0.20	0.20
160	0.20	0.20	0.20	0.20	0.20
180	0.20	0.20	0.20	0.20	0.20
200	0.20	0.20	0.20	0.20	0.20

Figure 3 (H) Adsorption isotherms for a carbon nanotube sample at 12.5, 20, 50, 100, and 150 °C.

### Summary

The K25 microbalance is a new commercial sorption instrument capable of performing measurements under extreme conditions. We have demonstrated excellent long term stability which makes the K25 suitable for uptake or release studies on small sample sizes.

We have demonstrated the ability to measure adsorption isotherms at temperatures up to 400 °C and pressures up to 1000 bar.

The K25 microbalance provides simultaneous determination of adsorption uptake and kinetic data using a single method.

M. Marcel, D. P. Dorem, R. L. Mordor, M. G. Roppe and M. J. Bentham  
Hiden Isochema Ltd., Warrington, U.K. info@hidenisochema.com

In this work, we present data measured under a range of challenging experimental conditions using a commercially available instrument, the K25 microbalance. The K25 is a high resolution microbalance, which can be used for a range of applications. Of particular note is, firstly, the practical requirement to be able to characterize materials under extreme conditions, such as high pressure and temperature, and secondly, by shales, which have highly heterogeneous material microstructures. Of 4 kg of shale, 10% of the weight is water, so the K25 is able to measure the effect of high pressures and elevated temperatures to mimic geological behavior [1-3].

Figure 4 shows (I) adsorption-desorption isotherms for a shale sample taken at 12.5, 20, 50, 100, and 150 °C, and then the sample was cooled back down to 12.5 °C, and the process repeated. The isotherms are very similar, demonstrating both the excellent long term stability of the K25 and the reliability of the data at these temperatures.

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Pressure (bar)	12.5 °C (mg/g)	20 °C (mg/g)	50 °C (mg/g)	100 °C (mg/g)	150 °C (mg/g)
0	0.00	0.00	0.00	0.00	0.00
20	0.05	0.05	0.05	0.05	0.05
40	0.10	0.10	0.10	0.10	0.10
60	0.15	0.15	0.15	0.15	0.15
80	0.20	0.20	0.20	0.20	0.20
100	0.20	0.20	0.20	0.20	0.20
120	0.20	0.20	0.20	0.20	0.20
140	0.20	0.20	0.20	0.20	0.20
160	0.20	0.20	0.20	0.20	0.20
180	0.20	0.20	0.20	0.20	0.20
200	0.20	0.20	0.20	0.20	0.20

Figure 4 (I) Adsorption-desorption isotherms for a shale sample at 12.5, 20, 50, 100, and 150 °C, and then the sample was cooled back down to 12.5 °C, and the process repeated. The isotherms are very similar, demonstrating both the excellent long term stability of the K25 and the reliability of the data at these temperatures.

Pressure (bar)	200 °C (mg/g)
0	0.00
20	0.05
40	0.10
60	0.15
80	0.20
100	0.25
120	0.20
140	0.20
160	0.20
180	0.20
200	0.20

Figure 5 (J) Adsorption isotherm on a coal sample at 200 °C. The curve shows a sharp increase in weight gain at approximately 100 bar, reaching a plateau around 0.2 mg/g.

Pressure (bar)	300 °C (mg/g)
0	0.00
20	0.05
40	0.10
60	0.15
80	0.20
100	0.25
120	0.20
140	0.20
160	0.20
180	0.20
200	0.20

Figure 6 (K) Adsorption isotherm on a coal sample at 300 °C. The curve shows a sharp increase in weight gain at approximately 100 bar, reaching a plateau around 0.2 mg/g.

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We have been busy this year promoting our new XEMIS microbalance and it continues to attract great interest from both new and existing customers. Talks have been given and posters presented at several international conferences including the

French Carbon Group meeting held in Orleans, France; at Characterization of Porous Solids (COPS-X), which was held in Granada, Spain and the Federation of European Zeolite Associations (FEZA) 2014 meeting held in Leipzig, Germany. In November Dr Darren Broom will be heading off to AIChE 2014 in Atlanta, USA, to present a poster entitled "A New Commercial Instrument for Gas Sorption Measurements Under Extreme Conditions", which features the latest XEMIS data produced in our in-house applications laboratory.