ANALYZER
HIDEN ISOCHEMA NEWSLETTER
ISSUE 13
WINTER 2022/23

HIDEN ISOCHEMA

Separating refrigerants using sorption

Two papers co-authored by a team at Hiden Isochema and published this year examined the separation of refrigerant mixtures using ionic liquids and zeolites.

Performed in collaboration with Professor Mark Shiflett at the University of Kansas, the work used Hiden Isochema's Integral Mass Balance (IMB) method, which allows determination of binary gas sorption isotherms as a function of gas phase composition at different fixed total pressures.

More on page 2...

Separating refrigerants using sorption

Since the phasing out of chlorofluorocarbon (CFC) refrigerants by the Montreal Protocol in 1987 and hydrochlorofluorocarbons (HCFCs) by the Copenhagen Amendment to the protocol in 1992, these harmful refrigerants have largely been replaced by hydrofluorocarbons (HFCs). HFCs are safe for the Earth's ozone layer, but some have a high global warming potential (GWP). As a consequence, in 2016, 197 countries signed the Kigali Amendment to the Montreal Protocol to phase out high GWP HFCs.

Many common HFC refrigerants are azeotropic or near-azeotropic blends, containing low GWP compounds, which can be separated and reclaimed, with the market potential for such recycling estimated at over a billion US dollars. Efficiently separating common refrigerant blends, such as R-410a (50/50 wt% HFC-32/HFC-125), is however challenging.

One solution is to use either absorption by ionic liquids (ILs) or adsorption in nanoporous materials.[1,2] In the first of the recent papers, Baca et al[3] reported the first measurements of binary absorption of HFC-32 and HFC-125 by two ILs for the purpose of separating R-410a using extractive distillation with IL entrainers. The second paper[4] reported the binary adsorption of HFC-32/HFC-125 on zeolite 5A for the purpose of performing the same separation using a process such as pressure swing adsorption (PSA).

Baca et al[3] used both an **IGA-003-MC** and a **XEMIS-003-MC** to measure binary HFC-32/HFC-125 isotherms in $[C_4C_1im][BF_4]$ and $[C_4C_1im][PF_6]$ at 298.15 K and a total pressure of 0.25 MPa. Both ILs preferentially absorbed HFC-32, but selectivities were found to be up to 35% higher in $[C_4C_1im][PF_6]$. Yancey et al,[4] meanwhile, used the **IGA-003-MC** and **XEMIS-003-MC** to measure binary HFC-32/HFC-125 isotherms on zeolite 5A at 298.15 K and a total pressure of 0.1 MPa. HFC-32 was adsorbed preferentially over HFC-125, with a selectivity of approximately 9.7, demonstrating that zeolite 5A is an excellent candidate for the adsorptive separation of R-410a.

Both studies were supported by the US National Science Foundation (NSF), under Grants 1920252 and 2029354, and they will form the basis for further development of processes for separating refrigerants using sorption.

More generally, measuring multicomponent gas sorption is challenging and these studies include the first data recorded using the IMB method implemented in a Hiden Isochema XEMIS gravimetric analyzer. A discussion of the practical issues and importance of further developing multicomponent gas sorption measurement methods and protocols can be found in an article published late last year in the magazine The Chemical Engineer.[5] For further information on Hiden Isochema products for measuring multicomponent sorption, meanwhile, please contact our applications team, info@hidenisochema.com

References

[1] D. K. J. A. Wanigarathna et al, Metal organic frameworks for adsorption-based separation of fluorocompounds: a review. Mater. Adv. 2020, 1 (3), 310–320.
[2] A. D. Yancey et al, Difluoromethane (HFC-32) and Pentafluoroethane (HFC-125) Sorption on Linde Type A (LTA) Zeolites for the Separation of Azeotropic Hydrofluorocarbon Refrigerant Mixtures. Langmuir, 2022, 38 (6), 1937–1953.
[3] K. R. Baca et al, First Measurements for the Simultaneous Sorption of Difluoromethane and Pentafluoroethane Mixtures in Ionic liquids Using the Integral Mass Balance Method. Ind. Eng. Chem. Res., 2022, 61 (27), 9774–9784.
[4] A. D. Yancey et al, Separation of Azeotropic Hydrofluorocarbon Refrigerant Mixtures: Thermodynamic and Kinetic Modeling for Binary Adsorption of HFC-32 and HFC-125 on Zeolite 5A. Langmuir, 2022, 38 (35), 10836–10853
[5] D. P. Broom, Separation Anxiety. The Chemical Engineer, 2021/2022, 966/7, 28-31.

MOST-H_2 Project Launch

Hiden Isochema is proud to be an associated partner in a Horizon Europe project, MOST-H_2, aiming to develop metal-organic frameworks (MOFs) for hydrogen storage.

The project will combine machine learning and synthetic chemistry to identify and synthesize new MOFs optimized for both gravimetric and volumetric capacity. The resulting materials will be incorporated in monoliths produced by Immaterial, a spin-out company from the University of Cambridge. Monolithic MOFs provide high volumetric capacities, compared to powders, and this will be exploited in scaled-up units designed and built by the Spanish pressure tank manufacturer Lapesa Grupo Empresarial, S. L. Life cycle assessment (LCA) will be performed and the use of the developed tanks analyzed for transport applications in the rail industry.

The MOST-H_2 consortium consists of 15 partners, from the UK, France, Spain, Italy, Germany, Austria, Greece and Morocco, and the project will run for 4 years, with total funding in the region of €6 million. MOST-H_2 is being coordinated by a team from NCSR "Demokritos", who recently hosted the first in-person meeting in Athens, Greece.

The Hiden Group Celebrate a Double Anniversary

2022 marked both Hiden Isochema's 20th anniversary, and Hiden Analytical's 40th anniversary.

Hiden Analytical was established in 1982 and has become a widely recognised name in the field of mass spectrometry. Hiden Isochema was formed in 2002, and is regarded as a market leader in the development and manufacture of gas and vapour sorption analyzers, but gravimetric sorption analyzers have been produced by Hiden since 1992, initially in collaboration with the University of Birmingham.

The Hiden group are proud to celebrate 40 years of continuous and independent operation, and Hiden Isochema are delighted to mark 20 years of ground-breaking product developments in sorption measurement technology.

Driven by customer and application focussed innovation, a unique and successful company culture and exemplary worldwide reputation has been gained. The group has global reach with offices in USA, China and Germany and representation remains strong throughout Europe, Asia and South America.

With the Hiden group now employing a talented staff of over 140 scientists, engineers, technicians and operations specialists at its UK headquarters, Hiden continues to go from strength to strength. Further company expansion includes new clean room facilities for precision assembly, a new vacuum/mechanical assembly suite and additional office space at both Hiden Analytical and Hiden Isochema's facilities in Warrington, UK, as well as comprehensive building renovations.

Original Hiden Mass Spectrometer

XEMIS 003 MC

PUBLICATION **ROUND-UP**

Hydrocarbon separation

Ultramicroporous Hydrogen-Bonded Organic Framework Material with a Thermoregulatory Gating Effect for Record Propylene Separation

Y. Chen, Y. Yang, Y. Wang, Q. Xiong, J. Yang, S. Xiang, L. Li, J. Li, Z. Zhang and B. Chen

J. Am. Chem. Soc., 2022. DOI: 10.1021/jacs.2c06585

Authors in China and USA describe a hydrogen bonded organic framework material, HOF-FJU-1, with exceptional ability to separate propylene (C_3H_6) from propane (C_3H_6). An **IGA-001** was used to measure gas sorption isotherms for CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, CO_2, N_2, and O_2. High resolution adsorption-desorption isotherms and sorption kinetics were recorded at 298, 313 and 333 K to characterize the single component adsorption processes. Breakthrough curves for 50:50 C_3H_6 / C_3H_8 mixtures were recorded using an **ABR**, at 6 temperatures from 298 to 333 K, at total pressures of 1 and 3 bar. The material, HOF-FJU-1 was shown to yield 99.5 % propylene purity from the 50:50 mixture; the performance being sustained over 20 cycles.

Zeolites

Gas Adsorption in Zeolite and Thin Zeolite Layers: Molecular Simulation, Experiment, and Adsorption Potential Theory

W. Kellouai, P. Judenstein, M. Plazanet, S. Baudoin, M. Drobke, A. Julbe and B. Coasne

Langmuir, 2022. DOI: 10.1021/acs.langmuir.1c03420

In this study reported by researchers in France, an **IMI-HTP** manometric gas sorption analyzer was used to measure methane adsorption isotherms for silicalite-1 zeolite powders, with the results used to validate a molecular simulation model. Isotherms were measured at range of temperatures and at pressures from 10^{-3} bar to 10^{2} bar, and correlated with previous literature results. The model was also applied to thin zeolite layers with different crystalline orientations and levels of surface flexibility. The results and the model are also discussed in relation to Polanyi's adsorption potential theory.

Carbon capture / carbons

Rational synthesis of microporous carbons for enhanced post-combustion CO_2 capture via nonhydroxide activation of air carbonised biomass

A. Altwala and R. Mokaya

RSC Advances, 2022. DOI: 10.1039/d2ra02661a

This paper describes the synthesis and characterization of microporous activated carbons derived from biomass, using potassium oxalate as the activating agent. Potassium oxalate is less corrosive and less toxic than more common hydroxide activating agents. The resulting carbons exhibited highly microporous structures. A **XEMIS** gravimetric sorption analyzer was used to measure CO_2 adsorption isotherms for the carbons, across a wide pressure range. Compared to equivalent hydroxide activated carbons, the potassium oxalate activated carbons show greater CO_2 uptake at pressures relevant to post-combustion CO_2 capture (i.e. close to atmospheric pressure); despite having lower CO_2 capacity at 20 bar.

Hybrid materials

Aligned macrocycle pores in ultrathin films for accurate molecular sieving

Z. Jiang, R. Dong, A. M. Evans, N. Biere, M. A. Ebrahim, S. Li, D. Anselmetti, W. R. Dichtel and A. G. Livingston

Nature, 2022. DOI: 10.1038/s41586-022-05032-1

An international collaboration, led by researchers at Imperial College London (UK), report an ultrathin polymer membrane film with impregnated aligned porous macrocyles. Alignment of the macrocycle is critical, and the resultant material has a tailored pore structure significantly better defined than typical polymer membrane films, and is therefore attractive for accurate molecular sieving applications. Amongst a range of characterization techniques, an **IGA-002** gravimetric sorption analyzer was used to measure vapor adsorption-desorption isotherms for water, methanol, acetonitrile, hexane and heptane; with the isotherm shape and magnitude of the sorption uptake for polar and non-polar solvents providing further evidence for the solvent separation properties of the material.

Discovering more. Seeing more.

DATE	CONFERENCE	LOCATION
26-27 January	**AFA (French Adsorption Association)**	Nancy, France
5-8 February	**ILSEPT (Ionic Liquids in Separation and Purification Technology)**	Scottsdale AZ, USA
22-23 February	**DZT (German Zeolite Meeting)**	Vienna, Austria
26-30 March	**ACS (American Chemical Society Spring Meeting)**	Indianapolis IN, USA
28-29 March	**TAC (Thermal Analysis Conference)**	Huddersfield, UK
27-30 March	**GFZ (French Zeolite Group Meeting)**	Obernai, France
3-5 April	**BZA (British Zeolite Association Meeting)**	Manchester, UK
22-25 May	**Interpore**	Edinburgh, UK
19-20 June	**UKPorMat (UK Porous Materials Conference)**	Sheffield, UK
2-6 July	**FEZA (Federation of European Zeolite Associations)**	Portorož-Portorose, Slovenia
3-6 July	**MC16 (RSC Materials Chemistry Conference)**	Dublin, Ireland

Dates are subject to change, please confirm details with event organizers.

Follow us on Twitter @HidenIsochema for our latest updates, research, materials science and anything else we find interesting!

Hiden Isochema Limited
422 Europa Boulevard, Warrington WA5 7TS
Tel: +44 (0) 1925 244 678 Email: info@hidenischema.com

hidenisochema.com