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A novel approach for the determination of sorption equilibria and sorption enthalpy used for MOF aluminium fumarate with water

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Abstract: Adsorption chillers are an environmentally friendly solution for the valorisation of waste or solar heat for cooling demands. A recent application is high efficiency data centre cooling where heat from CPUs is used to drive the process providing cold for auxiliary loads. The metal organic framework aluminium fumarate with water is potentially a suitable material pair for this low temperature driven application. A targeted heat exchanger design is a prerequisite for competitiveness requiring, amongst others, a sound understanding of adsorption equilibria and adsorption enthalpy. A novel method is used for their determination based on small isothermal and isochoric state changes applied with an apparatus developed initially for volume swing frequency response measurement to samples with a binder based adsorbent coating. The adsorption enthalpy is calculated through the Clausius-Clapeyron equation from the obtained slopes of the isotherm and isobar, while the absolute uptake is determined volumetrically. The isotherm confirms the step-like form known for aluminium fumarate with a temperature dependent inflection point at $p_{\mathrm{rel}} \approx 0.25$, 0.28 and 0.33 for 30, 40 and 60 °C. The calculated differential enthalpy of adsorption is 2.90±0.05 MJ/kg (52.2±1.0 kJ/mol) on average which is about 10–15% higher than expected by a simple Dubinin approximation.

Keywords: adsorption equilibrium; adsorption enthalpy; heat of adsorption; metal organic framework; aluminum fumarate; coating; adsorption; cooling; heat pump; heat transformation

1. Introduction

Adsorption chillers are an environmentally friendly solution for the valorisation of waste or solar heat for cooling demands. The working principle allows a simple, robust and scalable design. Adsorption chillers and heat pumps have been applied successfully for different applications like solar thermal cooling of buildings [1], gas adsorption heat pumps [2,3] and more [4,5]. A possible application that has attracted rising interest in recent years is the provision of data centre cooling driven by heat yielded from water cooled CPUs. Current high performance CPUs allow cooling water temperatures of up to 60 °C or more [6,7] that can be used to drive adsorption chillers.

An adsorption chiller (Figure 1) consists of two adsorption heat exchangers, a condenser and an evaporator in a pure working fluid atmosphere. If temperatures below 0 °C can be excluded, usually water is used as working fluid due to its high evaporation enthalpy. The adsorption heat exchangers (Ad-HX) have a heat transfer fluid on the primary and a stationary adsorbent material or composite on the secondary side. The process is cyclic: In the first half-cycle the CPU's waste heat is used to regenerate the first Ad-HX. The desorbed working fluid is condensed in the condenser which is cooled to the ambient at e.g. 30 °C. In the second half-cycle working fluid is adsorbed on the Ad-HX which is again cooled to the ambient. The resulting pressure drop induces the evaporation in the evaporator at about 20 °C. For continuous provision of cold, two Ad-HXs are operated alternately.

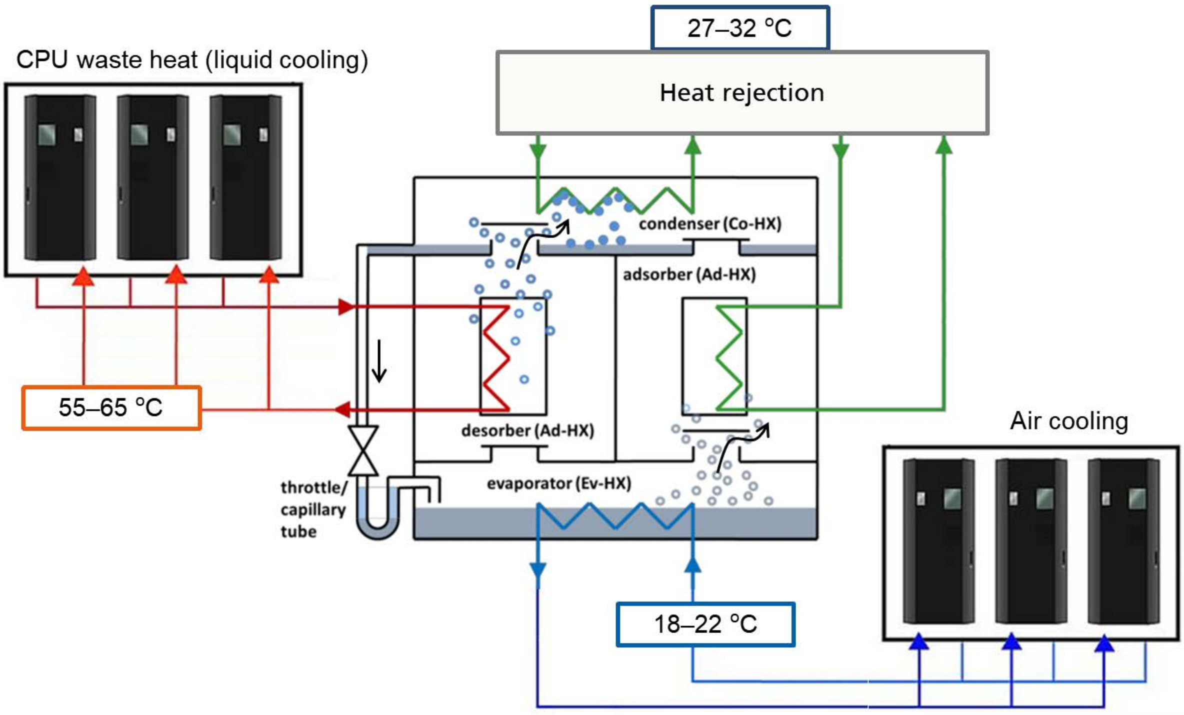

Figure 1: Working principle of an adsorption chiller for data centre cooling

Development of new adsorbent materials has been a research interest for many years [8]. Aluminium fumarate, a metal-organic framework (MOF) that attracted increasing interest for thermal applications in recent years, exhibits adsorption equilibrium properties that fit well to the boundary conditions of this cycle [9]. Due to its beneficial stepwise isotherm [8] it can allow considerably more efficient cycles compared to the state of the art material silica gel with a good hydrothermal cycle stability [10,11]. The material is potentially a low cost material due to widely available educts (Al-salts and fumaric acid) and water based synthesis route [12].

The increase of volume specific cooling power (VSCP) – thus reduction of specific costs – while keeping a reasonably high COP is one of the major development challenges for adsorption chillers [13]. Typical values for COPs of market available adsorption chillers are in the order of 0.5 to 0.65 [14]. In the case of data centre cooling the target COP is determined by the ratio of low temperature cooling demand and available waste heat from CPUs which typically is in the same range [6]. A promising approach to increase VSCP is to use binder based adsorbent coatings to allow for a substantially better heat transfer to the heat exchanger structure in comparison to loose grain bed, the state of the art solution [15]. Further performance increase can be reached through model based design and optimization which is more cost-effective than empiric trial-and-error prototyping as shown recently in a comprehensive overview on designing strategies for Ad-HX by Graf et al. [16]. However, model based design requires detailed knowledge of a) the adsorption equilibria, b) the adsorption enthalpy, c) relevant physical heat and mass mechanisms and the corresponding transfer coefficients, and d) the specific heat capacities, allowing for models with explicit dependency on design parameters like heat exchanger geometry, layer thicknesses and particle sizes. We developed a comprehensive approach to gain most of this data, i.e. a)–c), from small representative Ad-HX cutouts in a single measurement procedure based on

1. volumetric uptake measurement,
2. stepwise volume & temperature perturbation and
3. frequency response analysis.

In this paper we will focus on the first two steps for evaluating adsorption equilibrium and adsorption enthalpy. The frequency response analysis (FRA) for the investigation of heat and mass transfer processes builds upon this and will be dealt with in a following publication.

An apparatus developed initially for volume swing frequency response measurement also allows for measurements of the differential adsorption equilibrium, i.e. the slopes of the isotherm and the isobar, through the equilibrium response for small step experiments. Earlier the FRA setups were used for volume step experiments to evaluate sorption dynamics using a numerical non-linear transport model in the time domain [17] comparable to pressure jump [18,19] or temperature jump [20–22] experiments. We extend this approach to measuring the isobar slope with small temperature steps. Both slopes can be directly combined to determine the differential adsorption enthalpy at a specific thermodynamic state, i.e. adsorbent loading, temperature and pressure. Together with a calibrated dosing volume for the volumetric uptake measurement this allows for a comprehensive determination of sorption equilibrium, enthalpy and dynamics in a single automated measurement procedure.

2. Materials and Methods

2.1. Material

An aqueous dispersion (26.8 wt% aluminium fumarate (a.k.a. MIL-53(Al)-FA) Basolite® A520, BASF; 17.9 wt% SilRes® MP50E, Wacker Silicones) was processed by a knife coating applicator on 50x50x2 mm AlMg3 sample plates (Table 1). The wet film thickness was varied by an octagonal stainless steel mask with a defined thickness (200, 350, 600 µm) and constant coating surface A_{ct} (18.7 cm²). Samples were oven dried at 200 °C for 3 h before measuring coating thicknesses d_{ct} of final samples (Table 1, Figure 2) at five points with a probe indicator. The sample dry mass was determined by quickly ($T \geq 160$ °C) weighing the hot samples under lab atmosphere after oven drying. Total dry adsorbent content $w_{\mathrm{s,dry}}$ were first calculated from the suspension composition based on experimentally determined dry masses of different components as shown by Kummer et al. [23], and later cross checked by comparing the samples' uptake to the uptake of pure adsorbent powder measured volumetrically (AUTOSORB®, Quantachrome).

Figure 2: Sample Ct_610 with 0.61 mm coating thickness

Table 1: Sample mass and geometry, the adsorbent content was estimated when mixing the coating suspension and confirmed later by comparing the sample's uptake with the pure adsorbent powder isotherm (c.f. 3.1)

				By suspension composition		By comparison to pure adsorbent uptake	
Sample	m_{cmp} (mg)	d_{ct} (mm)	ρ_{cmp} (g/cm³)	$w_{\mathrm{s,dry}}$ (-)	w_{bnd} (-)	$w_{\mathrm{s,dry}}$ (-)	w_{bnd} (-)
Ct_140	134±3	0.14±0.04	0.51±0.15	0.75	0.25	0.72	0.28
Ct_240	217±4	0.24±0.05	0.48±0.10	0.75	0.25	0.79	0.21
Ct_610	563±11	0.61±0.07	0.49±0.06	0.75	0.25	0.80	0.20

2.2. Apparatus

Measurements are done with a custom setup (Figure 3) under pure water vapour atmosphere allowing vapour dosing as well as small volume and temperature steps. Moreover, the setup allows frequency response (FR), large temperature jump (LTJ), large pressure jump (LPJ) and small pressure jump (SPJ) experiments with water. Details on jump experiments with the setup have been reported extensively before [20,24,25], FR experiments will be published elsewhere.

The volume of the dosing chamber is constant ($V_{\mathrm{D}} = 41.815 \pm 0.021$ l) while the measurement chamber volume ($\bar{V}_{\mathrm{M}} = 885.4 \pm 1.3$ ml) can be varied by 4.12% through a mechanically driven vacuum bellow, while the bellow position is recorded with a vacuum stable linear variable differential transformer (Schreiber Messtechnik). The bellow position has been calibrated with a second order polynomial to the chamber volume by filling the evacuated and thermostated chamber with water of known mass. The sample is thermally well connected (thermal grease TG20032) to the cold plate kept isothermal ($\pm$ 0.01 K) by two switchable external circuits. The cold plate temperature is precisely measured with a 4-wired Pt100 sensor embedded in a bore. The chamber pressure is measured with a capacitive pressure transducer (MKS Baratron 627B, 0–100 mbar). Additionally, the sample's surface temperature is recorded using an IR temperature sensor (Heitronics KT15) through a ZnSe vacuum viewport with a noise equivalent temperature difference of 25 mK at 1 s response time. The measurement spot has a diameter of 6 mm (95%) and the detector's spectral response maximum is between 8 and 14 µm fitting to the transmissivity of the ZnSe viewport and the aimed sample temperature (20–80 °C). To minimise temperature gradients the whole vacuum setup is encapsulated in a temperature controlled cabinet ($\pm$0.1 K) set to the mean cold plate temperature. Data acquisition is done with a high precision digital multi meter (Agilent 34970A).

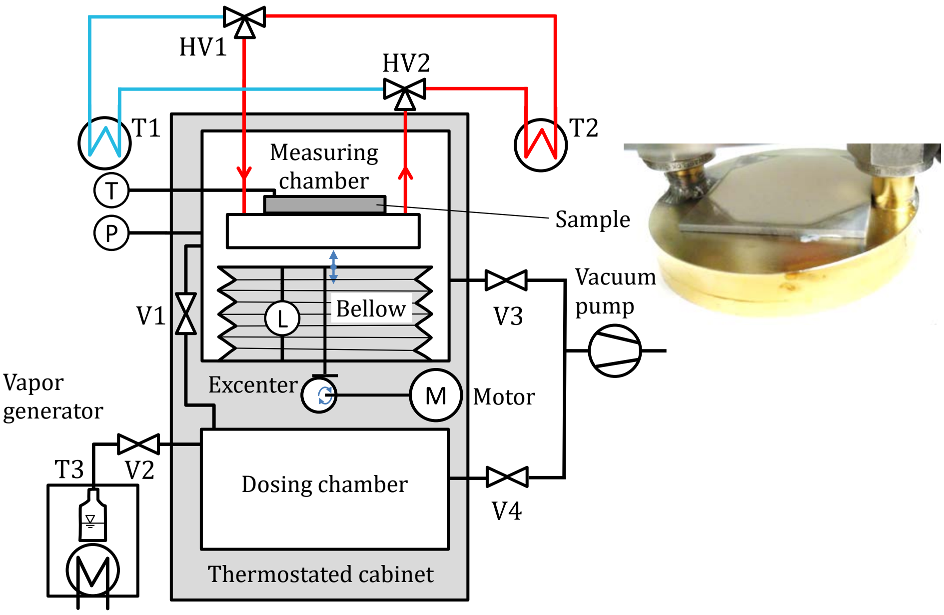

Figure 3: Sorption kinetic setup for frequency response, large temperature jump and large pressure jump experiments with absolute and differential equilibrium measurement. Absolute sorption equilibria are measured volumetrically by dosing in from the dosing chamber, differential equilibria by small temperature and pressure steps around equilibrium.

2.3. Procedure

The measurement procedure consists of two steps: pre-conditioning to the desired state and determination of equilibrium slopes. Throughout the measurement the temperature controlled cabinet is kept at the measurement mean temperature T_0.

Initially, samples were desorbed against a rotary vane pump ($p < 0.01$ mbar) at 95 °C overnight to remove any co-adsorbed impurities. For aluminium fumarate this ensures an initial loading X_{init} of 0 kg/kg. After cooling down the closed chamber to T_0 the sample is pre-conditioned to a desired loading X_0 by dosing in vapour from the dosing chamber. X_0 is calculated volumetrically from the mass balance of both chambers and the adsorbent dry mass m_s following the ideal gas law which is a very good approximation for water in the pressure and temperature region of the measurements:

$$X_0 = X_{\text{init}} + \frac{1}{T_0 R_{\text{w}} m_{\text{s}}}\left[V_{\text{D}} p_{\text{D1}} + V_{\text{M1}} p_{\text{M1}} - (V_{\text{M2}} p_{\text{M2}} + V_{\text{D}} p_{\text{D2}})\right]. \quad (1)$$

Here the indexes D and M denote the dosing and the measurement chamber where the volume depends on the bellow position. The pressures $p_{\text{D},1}$ and $p_{\text{D},2}$ are calculated beforehand based on the isotherm of the pure adsorbent powder to approximately reach the set point for X_0. The equilibrium pressure of the sample $p_0 = p_{\text{M},2}$ will follow the equilibrium of the sorbent at T_0 and X_0 yielding a point on the T_0-isotherm.

To determine the equilibrium slopes at the pre-conditioned sample state, the sample is exposed to small volume and temperature jumps symmetrically around V_0 and T_0 first by $\Delta V = 2\hat{V}$ with constant temperature and then by $\Delta T = 4$ K with constant volume. This allows determining the differential equilibrium, i.e. the slopes of the isotherm $\mathrm{d}X/\mathrm{d}p \approx (\Delta X/\Delta p)_T$ and the isobar $\mathrm{d}X/\mathrm{d}T \approx \left((\Delta X - \mathrm{d}X/\mathrm{d}p\Delta p)/\Delta T\right)_V$ from the equilibrium pressure difference Δp and loading change ΔX measured for the isothermal and the isochoric jump, respectively. A very slow drift in the pressure which is due to parasitic effects of the setup already reported before [24,25] is corrected by fitting linear models to equilibrium sections before and after the jump and using the extrapolated values at the centre. Finally, with both slopes the differential enthalpy of adsorption at X_0 and T_0 can be calculated based on Clausius Clapeyron's equation assuming ideal gas behaviour:

$$\Delta h_s \approx \frac{RT^2}{p}\frac{\mathrm{d}p}{\mathrm{d}T} = -\frac{RT^2}{p}\frac{\mathrm{d}X}{\mathrm{d}T}\left(\frac{\mathrm{d}X}{\mathrm{d}p}\right)^{-1} \quad (2)$$

Loading, differential equilibrium and adsorption enthalpy are important input parameters for a subsequent FRA reported elsewhere. Integration in a single measurement routine allows for measurement under exactly the same conditions (in-situ). As the sample is pre-conditioned only once this eliminates the need for time consuming external measurements and possibly error prone transfer to the measurement conditions.

To exclude a local hysteresis of the adsorption equilibrium, an important pre-requisite for FRA, a further test is included in the routine: The same equilibrium state X_0, T_0 is reached coming from a small and from a larger volume at constant temperature and vice versa. The equilibrium loading is then compared and a "hysteresis-free" behaviour assumed if the loading difference between the two directions is below the measurement uncertainty.

2.4. Uncertainty evaluation

Uncertainty analysis has been carried out based on [26] including uncertainty from sample variance (type A) and uncertainties from imperfect calibration and correction (type B).

The uncertainty of the mean values are between 0.4 ml (20 °C) and 1.3 ml (80 °C) for V_0, between 0.05 mbar ($p_0 = 5$ mbar) and 0.15 mbar ($p_0 = 100$ mbar) for the chamber pressure and about 0.1 K for the mean sample temperature T_0. Typical uncertainties for vapour dosing are in the order of 1 to 4 mg influenced mainly by p_0 for 10 to 60 mbar. Thus, uncertainties for the loading are smaller for higher sample dry mass given constant dry mass uncertainty.

3. Results and Discussion

Results are reported for five different loadings at 40 °C and one loading at 30 and 60 °C, respectively.

3.1. Adsorption equilibrium

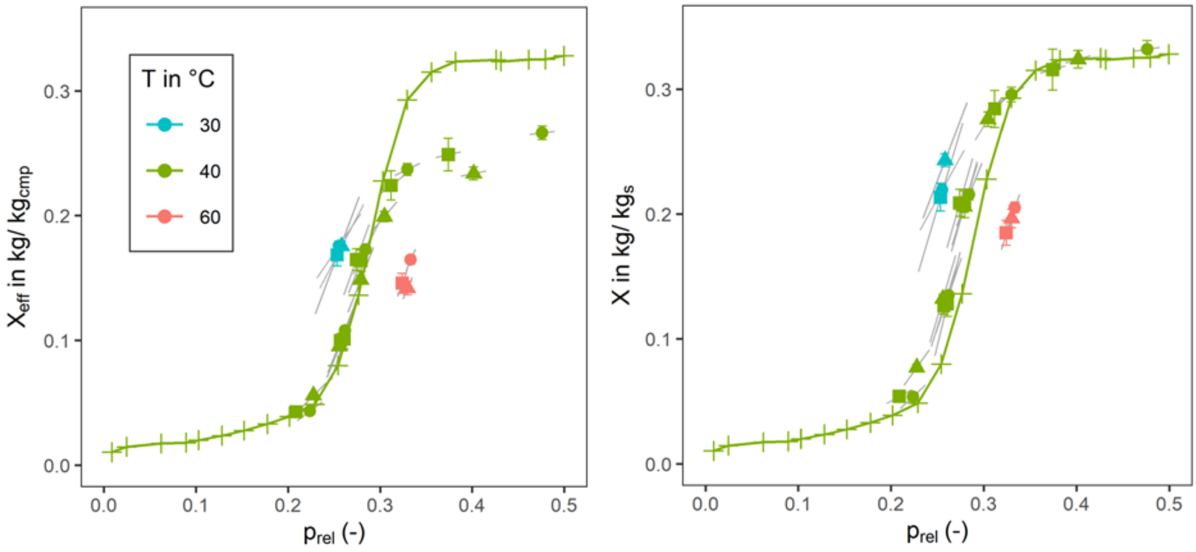

Figure 4: Equilibrium points measured for Ct_140 (▲), Ct_240 (■) and Ct_610 (●) at 30, 40 and 60 °C in comparison with the 40 °C isotherm of the initial pure adsorbent powder (+), based on total sample dry mass (left) and adsorbent mass determined by uptake correction (right); the grey lines indicate the local equilibrium slope measured by small volume jumps

The water isotherm of the adsorbent powder at 40 °C (Figure 4) shows the characteristic step-like uptake to a plateau at 0.32 kg/kg and is in line with [11] or slightly lower than [10,27] previous results. The position of the step is temperature dependent with an inflection point at $p_{\mathrm{rel}} \approx$ 0.25, 0.28 and 0.33 for 30, 40 and 60 °C. Measured local isotherm slopes are in agreement with the tangent for 40 °C. The position of the uptake step is reproducible within the samples and shows a strong temperature dependency that persists when applying a Dubinin transformation [28]. Hence, the assumption of a temperature invariant characteristic curve is a strong simplification for aluminium fumarate and should be applied with care. The exact position of the uptake step is an important information for application as it determines the available driving forces and finally the resulting equipment power [3].

No significant hysteresis was observed, neither locally by the procedure explained before (2.3) nor globally. For the later the vapour dosing procedure was modified starting with saturated sample ($p_{\mathrm{rel}} = 0.5,\ T = 40$ °C, $X = 0.33$ kg/kg$_S$) and desorbing into the dosing chamber. Probably, the hysteresis found in previous results was due to incomplete equilibrium and/or pore condensation occurring at $p_{\mathrm{rel}} \gg 0.5$ which was disregarded here due to the limited relevance for heat transformation applications.

The adsorbent content calculated by comparing the uptake of sample to the powder (Figure 4, right) fits on average the values calculated at sample preparation (Table 1) showing that the binder has no significant influence on adsorption equilibrium. The results show good agreement between the two thicker samples and a slight deviation of the thinnest sample Ct_140, which could be explained by a slightly lower adsorbent content of the coating. The difference to the uptake of the pure adsorbent can be explained by the inert binder/loss due to the coating process, differences in the production process and measurement uncertainty of the volumetric adsorption measurement.

A general description of the measured sorption equilibrium for modelling purposes is given in the supplement (S1).

3.2. Adsorption enthalpy

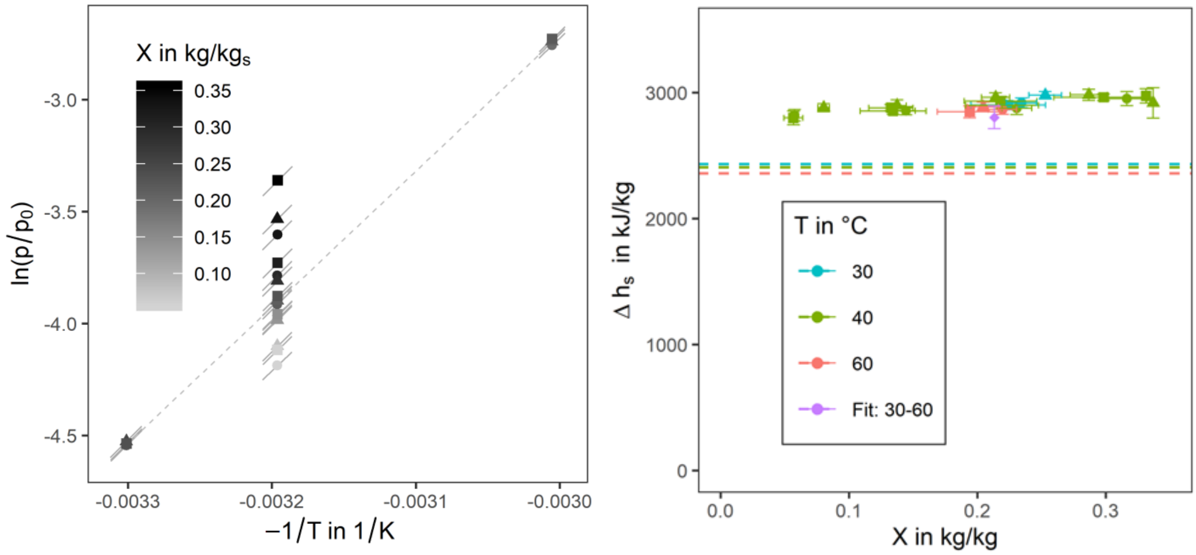

Figure 5: Left: Clausius-Clapeyron plot (p_0 = 1 bar) with measured equilibrium points for different samples (▲ Ct_140, ■ Ct_240, ● Ct_610) and isostere slope calculated from measured local deviations (short grey lines) and linear fit of points with $X_{\mathrm{eff}} \approx 0.16$ kg/kg (- - -), uncertainties of T and p are bellow point size; Right: differential adsorption enthalpy calculated from isostere slopes of local equilibria and 0.2-kg/kg-fit over corrected loading with the evaporation enthalpy of water (- - -)

The calculated differential enthalpy of adsorption is 2.90±0.05 MJ/kg (52.2±1.0 kJ/mol) on average. The calculation with Eq. (2) is based on either the local equilibrium slope indicated in Figure 5 or on a linear fit of the quasi-isosteric points ($X_{\mathrm{eff}} \approx 0.16$ kg/kg) measured at 30, 40 and 60 °C. The Clausius-Clapeyron plot shows that local slopes coincide well with the multi-temperature fit, and so do the calculated enthalpies. Temperature and loading dependencies are negligible in the parameter range evaluated. The adsorption enthalpy is about 10–15% higher than expected by a simple Dubinin approximation (sum of evaporation enthalpy at the same temperature and the adsorption potential $A = -RT\ln(p_{\mathrm{rel}})$, [28]) which is in qualitative accordance to the observed temperature variance of the isotherm. Thus, the application of the concepts of a characteristic curve for the description of the sorption equilibrium and of the adsorption potential for the sorption enthalpy result in a crude approximation for the case of aluminium fumarate.

4. Conclusions

In this work we developed a novel method for in-situ measurements of sorption equilibria and enthalpy in an apparatus dedicated to the sorption dynamic measurement. The method, based on dosing vapour from calibrated volumes and small temperature and volume steps around an equilibrium point, allows for direct measurements of the isobar's and isotherm's slope tightly around a specific thermodynamic state. This allows extracting the loading and temperature dependency of the isostere's slope and thus the sorption enthalpy.

The method was tested on samples coated with a composite of aluminium fumarate particles with Silres® as a binder in different thicknesses (140–610 µm) at 30–60 °C and the entire loading range. The measured sorption equilibrium fits expectations from the pure adsorbent powder's isotherm and the coating composition. The coating procedure did not alter the adsorption properties.

The measurement of the differential adsorption enthalpy was successfully verified by comparing the local slope of the isostere to the linear regression over the whole temperature range. The sorption enthalpy is 2.90 ±0.05 MJ/kg (52.2 ±1.0 kJ/mol) on average with no significant dependency with either loading or temperature.

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1, Section S1: General description of the sorption equilibrium of aluminium fumarate.

Author Contributions: Conceptualization, E.L. and G.F.; methodology, E.L.; software, E.L.; validation, G.F. and L.S.; formal analysis, E.L.; investigation, E.L.; resources, E.L.; data curation, E.L.; writing—original draft preparation, E.L.; writing—review and editing, G.F., L.S. and G.S.; visualization, E.L.; supervision, G.F., L.S. and G.S.; project administration, G.F.; funding acquisition, E.L., G.F., L.S. and G.S. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

5. Nomenclature

5.1. Abbreviations

Ad-HX	Adsorber heat exchanger

5.2. Variables

T	Temperature (K)
p	Pressure (Pa)
X	Loading ($kg_{adsorbed}/kg_{sorbent,dry}$)
X_{eff}	Effective loading ($kg_{adsorbed}/kg_{composite,dry}$)
V	Volume (m^3)
A	Surface area (m^2), adsorption potential (J/kg), Amplitude (any unit)
R	Universal gas constant (J/(mol K))
R_w	Specific gas constant of water (J/(kg K))
m	Mass (kg)
t	Time (s)
M	Molar mass (kg/mol)
Δh_s	Differential adsorption enthalpy ($J/kg_{adsorbed}$)

5.3. Indices

w	Water
s	(Ad)sorbent, (ad)sorption
0	Temporal mean value
D	Dosing chamber
M	Measurement chamber
V	At constant volume
T	At constant temperature
ch	(Measurement) chamber
cmp	Composite
ct	Coating
rel	Relative

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