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Thermodynamic characterisation of adsorptive gas/adsorbent systems using the ALI^c-model

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Abstract The ALI^c-Model is a thermodynamically consistent pore filling model which allows microporous and mesoporous adsorptive gas/adsorbent systems to be described and compared directly. Examples of this will be shown on 20 systems. To this end, the standard-molar-free-enthalpy of adsorption is divided into a material-specific concentrate term and a geometric mixing term. At standard pressure and boiling temperature, all the curves of the standard-molar-free-enthalpy of adsorption as a function of the degree of pore filling end at the point of free-enthalpy of adsorption = 0 and at the degree of pore filling = 1. From these characteristic curves, finite molar values for free-enthalpy, enthalpy and entropy of adsorption can be calculated for the adsorbate-concentrate at a negligible degree of pore filling. Alkanes on activated carbons and CO$_2$ on Zeolite 5A are used as demonstrating examples. These values and curves obtained from measurement of adsorption-isotherm-fields enable the interaction of the adsorbate with the adsorbent to be characterized, thus providing additional information for adsorption processes and for the development of adsorbents.

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List of symbols

$A(\Xi)$	Polanyi potential
m_i	Mass of component i (kg)
MW	Molecular weight (g/mol)
n_i	Mol of component i (mol)
p_i	Partial pressure of component i (bar)
T	Temperature, absolute (K)
T_B	Boiling temperature at 1 bar (K)
T_S	Boiling temperature of the vapour pressure curve
V	Volume under standard conditions (m_N^3)
V_{ads}	Specific accessible geometric adsorption volume (ml/100 g)
$X_i = m_i/m_s$, $X_{i,\max} = m_{i,\max}/m_s$	Mass loading of adsorbent s by adsorptive gas i (g/100 g)
ΔH	Difference in molar-enthalpy (J/mol)
ΔS	Difference in molar-entropy (J/(mol K)
ΔG	Difference in molar-free-enthalpy (J/mol)
$\beta(T) = \frac{1}{V_m(T,p)} \cdot \left(\frac{\partial V_m}{\partial T}\right)_p$	Isobaric volume expansion coefficient ($1/K$)
ρ	Density (kg/m^3)
$\Xi = X_i / X_{i,\max}$	Degree of pore filling (−)

R	General molar gas constant $(8,314\,\frac{\mathrm{J}}{\mathrm{mol\,K}})$
ACC	Activated carbon fibre cloth (−)

Superscripts

isochor	Isochoric
std	Standard

Subscripts

a	In relation to the substance to be adsorbed
as	In relation to the adsorbed substance
ads	In relation to adsorption
abs	Absolute
B	In relation to standard boiling pressure of 1 bar
$crit$	Critical
con	In relation to condensation
$Conc$	In relation to the concentrate
$excess$	Excess
i	Component i, general
liq	In relation to the liquid phase
max	Maximum
mix	In relation to mixing
$mean$	In relation to a mean value
$0AA$	In relation to the degree of pore filling 0, adsorbate, adsorbed substance
s	In relation to the adsorbent
S	In relation to the liquid–vapour equilibrium
std	Standard
exp	Fitting parameter, exponential
$h{\cdot}ex$	Fitting parameter, exponential in terms of H
$s{\cdot}ex$	Fitting parameter, exponential in terms of S

1 Fundamentals of the ALI^c-Model

The so called Adsorbate-Liquid-Isotherm-(ALI)-Model described in (Schippert and Kimmerle 2008a, b, 2009a, b; Kimmerle and Schippert 2011) is extended above the critical temperature $T_{crit.}$ by a hypothetical reference vapor pressure and then called ALI^c-Model.

1.1 Task definition

There are considerable theoretical and application-related shortcomings in models for gas phase adsorption on microporous and mesoporous adsorbents. This opinion is also shared by colleagues such as (Shivaji and Ramesh 1981; Chiang et al. 2001; Myers 2003; Ramirez et al. 2005; Karge and Weitkamp 2008; Lopatkin et al. 2007). Tóth and József (2002) points out that more than 100 adsorption isotherm equations exist that are only suitable for certain applications, each. He believes that it might be possible to find a thermodynamically consistent theory for most of these equations. According to Shivaji and Ramesh (1981) for example, two criteria are necessary for a good model; the first is an extensive pressure and temperature range to allow application in process design and the second is the lowest possible number of model parameters. The ALI^c-Model described in this article is intended to fulfill the following ten demands and requirements:

1. The ALI^c-Model describes the adsorption process in pores.
2. The adsorbent is a porous, rigid and inert body.
3. The ALI^c-Model distinguishes between the gas phase and the adsorbate phase. The density in the adsorbate phase is always higher than in the gas phase, both, inside and outside the pore. The density in the adsorbate phase inside the pore has a gradient.
4. No negative excess loading exists in the ALI^c-Model.
5. The ALI^c-Model is a model of pore filling with the degree of pore filling $0 \leq \Xi \leq 1$. For $T < T_{crit.}$ the pore is entirely filled at the saturated vapor pressure of the adsorptive gas. At low degrees of pore filling, the ALI^c-Model merges into the Henry isotherm.
6. The free-enthalpy of adsorption depends on the temperature and degree of pore filling. As for adsorption in the subcritical temperature range, the standard free-enthalpy, the enthalpy and the standard-entropy of adsorption have to be equal to the corresponding values for condensation, when the pores are filled.
7. The adsorption entropy is divided into the characteristic entropy of bonding and the “geometric” entropy of mixing.
8. The mixing process between the occupied adsorption sites and the massless unoccupied adsorption sites is athermal (Schippert and Kimmerle 2008b).
9. The thermodynamic functions of the free-enthalpy of adsorption should be continuous during the transition from the subcritical to the supercritical range.
10. A hypothetical reference vapor pressure is defined by linear extrapolation of the standard-free-enthalpy of condensation for $T < T_{crit.}$.

1.2 Description of the ALI^c-Model

The main issue for the practical application of adsorption isotherms in industry is generally how much adsorptive gas (a) is adsorbed as an adsorbate (as) in [kg_{as}, mol_{as}] on the adsorbent (s) at a given partial pressure p_a. Therefore, most of the isotherm equations used to describe measured values, express adsorbent loading $X = n_{as}/m_s$ in [mol_{as}/kg_s] or the adsorbent mass fraction [kg_{as}/kg_s] as a function of the partial pressure p_a of the adsorptive gas and sometimes of the temperature T, hence

$$X = X(T, p_a). \tag{1}$$

In contrast, the ALI^c-Model firstly focuses on the level of partial pressure p_a that prevails under equilibrium conditions at a certain degree of pore filling Ξ and at a given temperature T which means that the isotherms take the form

$$p_a = p_a(T, \Xi). \tag{2}$$

In this case, the degree of pore filling Ξ is defined as the relationship of the adsorbate volume V_{as} to the adsorption volume V_{ads} with the greatest possible access for the adsorbate in question, expressed as $\Xi = V_{as}/V_{ads}$ in, for example $[ml_{as}/ml_{ads}]$, and has values from 0 to 1 (Seliverstova et al. 1986; Dubinin et al. 1993). Consequently, the specific adsorption volume $v_{ads} = V_{ads}/m_s$, accessible for the adsorbate, does not necessarily have to be equal to the specific pore volumes from N_2/CO_2 adsorption measurements or helium gas pycnometry. This is true particularly for adsorptive gases with large molecule volume. In order to determine the material-specific volume with the greatest possible access for the adsorbate $v_{ads}(T, p_S, X_{\max}) = v_{as,\max} = X_{as,\max}(T, p_S)/\rho_{a,liq}(T, p_S)$, maximum loading $X_{as,\max}(T, p_S)$ can be measured experimentally as a function of temperature and calculated using the density of the liquid $\rho_{a,liq}(T, p_S)$ at saturated vapor pressure. A second determination method is obtained, when the measured results are fitted. Then, the material-specific volume can be used as a adjustable parameter and the measured results are the initial starting values.

Consequently, the ALI^c-Model is a model of pore filling, e.g. similar to the D–A isotherm equation (Dubinin and Astakhov 1971) often applied in practice. It is assumed that the adsorbent is a porous, rigid, inert body with negligible coefficients of compression and temperature expansion. Its thermodynamic variables of state are not changed by the adsorption process. This means that all changes of free-enthalpy, enthalpy or entropy of adsorption are shifted to the transition adsorptive gas → adsorbate. The basic principles of the D–R isotherm equation (Dubinin and Radushkevitch 1947) and the D–A isotherm equation (Dubinin and Astakhov 1971) are summarized in (Hutson and Yang 1997). The two equations are only valid from a pore filling degree of $\Xi > 0.15$ and they are not thermodynamically consistent because the requirement for a linear slope at $\Xi \to 0$ in the Henry range is not fulfilled. The same is true for the further development of these equations, namely the D–R–S isotherm equation (Dubinin and Stoeckli 1980) and the J–C isotherm equation (Jaroniec et al. 1989). The studies by Chen and Yang (1994) ultimately resulted in the C–Y equation that can be applied from $\Xi > 0.1$. Owing to experience, it can be assumed that the adsorption volume is entirely filled at sub-critical temperature $T < T_{crit.}$ and at the saturated vapor pressure of the adsorptive gas. Hence the degree of pore filling then is $\Xi = 1$ as is the case for the D–A isotherm equation but not for the Langmuir isotherm equation (Hutson and Yang 1997).

The ALI^c-Model distinguishes between the adsorbate phase and the gas phase inside the pore. The partial pressure and density of the gas phase are equal to the gas density outside the pore. The criterion for distinguishing between the adsorbate phase and the gas phase inside the pore is solely the density in each case. The adsorbate phase has a greater density than the density of the gas phase calculated by an equation of state. At supercritical temperatures $T > T_{crit.}$, for each level of bonding energy exists a temperature and pressure, for which the differential density of the adsorbate $\rho_{as}(T, \Xi)$ is equal to the gas density of the gas phase $\rho_a(T \geq T_{crit.})$. Distinguishing between the adsorbate phase and the gas phase is meaningless from this temperature and pressure. By comparison to the evaporation of pure substances, this temperature can be referred to as the “critical temperature” $T_{crit.ads}(\Xi)$ or the “critical pressure” $p_{crit.ads}(\Xi)$ of the adsorbate. The “adsorbate” is then present in a density equal to the gas density $\rho_a(T \geq T_{crit.}, p)$. Hence, no negative excess loading occurs in the ALI^c-Model. Wherever the critical temperature of the adsorbate has been exceeded in the pore, adsorption no longer takes place.

This approach allows the adsorbate for each degree of pore filling Ξ to be considered and treated as a separate “adsorbate-liquid” with a separate vapor pressure curve in each case. Figure 1 shows the adsorption isotherm field for toluene on ACC Chemviron. The dots represent measured values while the lines were fitted using the ALI^c-Model. It is shown in this example for a pore filling degree of 30 %, how the vapor pressure curve for the adsorbate-liquid is obtained. The model presented in this article is referred to as the adsorbed-liquid-isotherm-(ALI^c)-Model, where “c” stands for the fact that the adsorption can be considered above the critical temperature, in contrast to earlier works by the authors (Schippert and Kimmerle 2008a, b, 2009a, b; Kimmerle and Schippert 2011).

A feature particular to the ALI^c-Model is the partition of the adsorption entropy into a “geometric” entropy term and a “bonding” entropy term, characteristic for the adsorption system. In this case, the term “bonding” is used to describe the phase transition from the gas phase to the adsorbate phase at standard pressure. As far as the reference pressure and reference temperature are concerned, the bonding entropy term is a separate characteristic value for each adsorptive gas/adsorbent system and it allows different systems to be compared directly if an appropriate reference temperature is chosen.

The geometric entropy term describes the increase in entropy caused by distribution or dilution of the

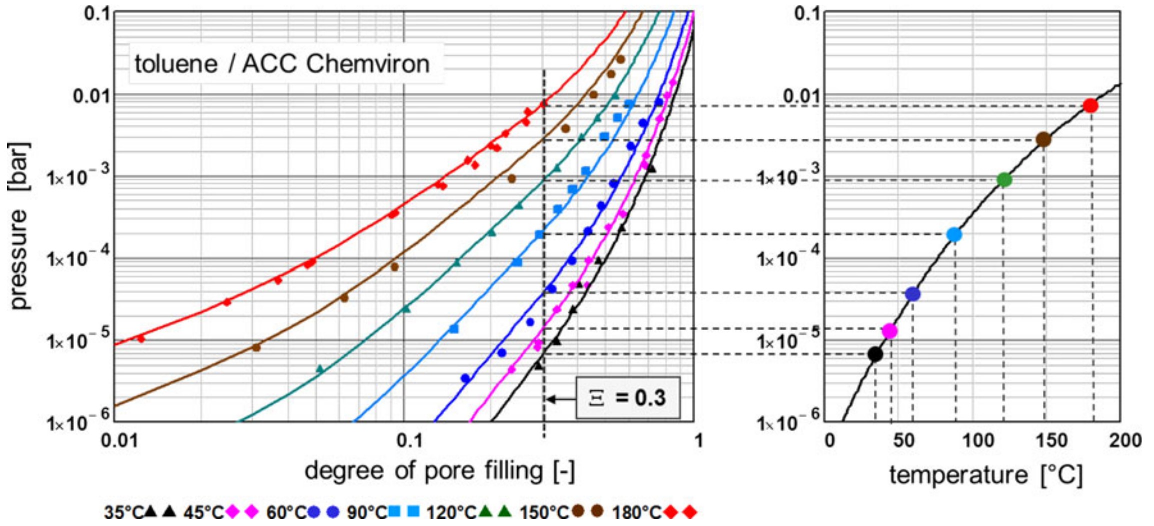


Fig. 1 Adsorption isotherm field for Toluene on ACC Chemviron. The dots are measured values (Schippert 2003), the lines have been fitted with the ALI^c-Model. At a degree of pore filling of $\Xi = 0.3$ it is demonstrated, how a vapor pressure curve for the adsorbate-liquid can be obtained. Such vapor pressure curves can be constructed for each degree of pore filling

"concentrated" adsorbate-liquid, a hypothetical "adsorbate-concentrate", over the adsorption sites of the entire adsorbent. This process could also be interpreted as a mixture of the adsorbate-concentrate and the "diluted-liquid", consisting of the unoccupied massless adsorption sites. Figure 2 shows the mixing process and the distribution or dilution of the adsorbate-concentrate with the diluate to become the adsorbate-liquid. A degree of pore filling of 40 %, i.e. $\Xi = 0.4$ was chosen. This entropic term is not material-specific but rather only depends on the degree of pore filling Ξ (Schippert and Kimmerle 2008b).

1.3 Excess and absolute loading

The relation between absolute loading $X_{abs}(T, \Xi)$ and the degree of pore filling Ξ is obtained from the average density of the adsorbate $\bar{\rho}_{as}(T,\Xi)$ and the specific adsorption volume v_{ads} that can be accessed by the adsorbate or from the temperature-dependent maximum loading $X_{\max}(T)$, because it is true that

$$X_{abs}(T,\Xi) = v_{ads} \cdot \bar{\rho}_{as}(T,\Xi) \quad \text{and} \quad \Xi(T,X) = \frac{X_{abs}(T,\Xi)}{X_{\max}(T)} \tag{3}$$

The temperature-dependent maximum loading $X_{\max}(T)$ can be measured. In this case, the average density of the adsorbate $\bar{\rho}_{as}(T,\Xi)$ and its thermal coefficient of expansion β_{as} can be calculated at $\Xi = 1$, when the specific adsorption volume v_{ads} is known. If a constant, temperature-independent, specific adsorption volume v_{ads} is assumed for a certain adsorbate, the average adsorbate density and its temperature dependence determined from the measurements, have to be consistent with the adsorbate density calculated by isotherm fitting using the ALI^c-Model.

For low temperature ranges far above the "critical temperature" of the adsorbate-concentrate, it can be assumed that the thermal coefficient of expansion β_{as} for the adsorbate is constant (Seliverstova et al. 1986) so that the following exponential statement is justified

$$X_{\max}(T) = v_{ads} \cdot \bar{\rho}_{as}(T_{std}) \cdot e^{\beta_{as}(T - T_{std})}. \tag{4}$$

Thus, for the system under analysis, the thermal coefficient of expansion β_{as} and the product of v_{ads} and $\bar{\rho}_{as}(T_{std})$ can be regarded as a constant model parameter. Since the pressure-dependent absolute loading X_{abs} is a unique function, in contrast to the pressure-dependent excess loading X_{excess}, the loading values for data adjustment,

Fig. 2 Illustration of the mixing, distribution or dilution process of the "adsorbate-concentrate" with the "diluate" to form the "adsorbate-liquid". A degree of pore filling of 40 %, i.e. $\Xi = 0.4$ is used in the example

determined from the measurement values, have to be converted using

$$X_{abs} = X_{excess} \cdot \left(1 - \frac{\rho_{gas}(T,p)}{\bar{\rho}_{as}(T,\Xi)}\right)^{-1}. \tag{5}$$

For high pressures >5 bar in the ALI^{c} equations, the average density of the adsorbate $\bar{\rho}_{as}(T_{std})$ has an enormous effect on the quality of the adjusted data for high pressures.

2 Thermodynamics of the ALI^{c}-Model

2.1 Standard-molar-free-enthalpy of adsorption

With the enthalpy $\Delta H_{con}(T)$ and the entropy $\Delta S^{p_{std}}_{con}(T)$, the differential standard-molar-free-enthalpy $\Delta G^{p_{std}}_{con}(T)$ of condensation at the standard pressure of 1 bar is expressed as

$$\Delta G^{p_{std}}_{con}(T) = \Delta H_{con}(T) - T \cdot \Delta S^{p_{std}}_{con}(T) = R \cdot T \cdot \ln\left(\frac{p_S(T)}{p_{std}}\right) \tag{6}$$

Similarly, with the enthalpy $\Delta H_{ads}(T, \Xi)$ and the entropy $\Delta S^{p_{std}}_{ads}(T,\Xi)$, the differential standard-molar-free-enthalpy $\Delta G^{p_{std}}_{ads}(T,\Xi)$ of adsorption at the standard pressure of 1 bar is expressed as

$$\begin{aligned}\Delta G^{p_{std}}_{ads}(T,\Xi) &= \Delta H_{ads}(T,\Xi) - T \cdot \Delta S^{p_{std}}_{ads}(T,\Xi) \\ &= R \cdot T \cdot \ln\left(\frac{p(T,\Xi)}{p_{std}}\right).\end{aligned} \tag{7}$$

As was the case with the original ALI-Model (Schippert and Kimmerle 2008b), the standard-molar-free-enthalpy of adsorption is divided into a geometric mixing term $\Delta G_{ads.mix}(T,\Xi)$ and a material-specific concentrate term $\Delta G^{p_{std}}_{ads.Conc}(T,\Xi)$ resulting in

$$\Delta G^{p_{std}}_{ads}(T,\Xi) = \Delta G_{ads.mix}(T,\Xi) + \Delta G^{p_{std}}_{ads.Conc}(T,\Xi). \tag{8}$$

The partition of $\Delta G^{p_{std}}_{ads}(T,\Xi)$ into an enthalpic term and an entropic term for the adsorbate-concentrate, which was introduced in the original ALI-Model already at this stage, has been abandoned, as has the division into condensation-independent and temperature-independent bonding terms, because this led to contradictions over very wide temperature ranges in particular, close to the critical temperature. In addition this allows one parameter to be saved for the fitting of the measured values and prevents ambiguity in data adjustment, such as the mutual compensating effects of enthalpic and entropic terms.

It does not seem effective to divide $\Delta G^{p_{std}}_{ads}(T,\Xi)$ into the temperature-independent Polanyi potential $A(\Xi)$ (Polanyi 1914, 1916, 1932) as is the case for the D–R isotherm equation (Dubinin and Radushkevitch 1947) and the D–A isotherm equation (Dubinin and Astakhov 1971) and into the temperature-dependent differential standard-free-enthalpy of condensation $\Delta G^{p_{std}}_{con}(T)$ at the standard pressure of 1 bar, hence $\Delta G^{p_{std}}_{ads}(T,\Xi) = R \cdot T \cdot \ln\left(\frac{p(T,\Xi)}{p_{std}}\right) = \underbrace{R \cdot T \cdot \ln\left(\frac{p_S(T)}{p_{std}}\right)}_{\Delta G^{p_{std}}_{con}(T)} + \underbrace{R \cdot T \cdot \ln\left(\frac{p(T,\Xi)}{p_S(T)}\right)}_{-A(\Xi)}$ and

$$\Delta G^{p_{std}}_{ads}(T,\Xi) = \Delta G^{p_{std}}_{con}(T) + A(\Xi). \tag{9}$$

Besides other disadvantages, the bonding terms for example, would be temperature-independent, which runs contrary to experience.

At an assumed athermal mixing of the ALI^{c} concentrate with the massless unoccupied adsorption sites that is $\Delta H_{ads.mix}(T,\Xi) = 0$, $\Delta G_{ads.mix}(T,\Xi) = T \cdot \Delta S_{ads.mix}(T,\Xi)$, is obtained. The geometric mixing term, derived in Schippert and Kimmerle (2008b), can be applied and the following expression is obtained

$$\begin{aligned}\Delta G^{p_{std}}_{ads}(T,\Xi) &= \Delta G^{p_{std}}_{ads.Conc}(T,\Xi) + R \cdot T \\ &\quad \cdot \ln\left(\Xi \cdot (1-\Xi)^{\frac{1-\Xi}{\Xi}}\right) \\ &= R \cdot T \cdot \ln\left(\frac{p(T,\Xi)}{p_{std}}\right).\end{aligned} \tag{10}$$

Thus, the standard-molar-free-enthalpy of adsorption for the adsorbate-concentrate $\Delta G^{p_{std}}_{ads.Conc}(T,\Xi)$ can be calculated directly from the measured isotherm values, if the relationship between the degree of pore filling Ξ and absolute loading X is known. Moreover, the mathematics used for description purposes have to be formulated in such a way that the general conditions derived from the demands and requirements are fulfilled.

Below the critical temperature and when the pores are completely filled $\Xi = 1$, the differential standard-molar-free-enthalpy of adsorption for the adsorbate is equal to that of the adsorbate-concentrate, because the mixing entropy is $\Delta S_{ads.mix}(T,\Xi=1) = 0$. In accordance with the concept for the ALI^{c}-Model, they are also equal to the standard-molar-free-enthalpy of condensation $\Delta G^{p_{std}}_{con}(T)$ and therefore it is

$$\Delta G^{p_{std}}_{ads.Conc}(T,\Xi=1) = \Delta G^{p_{std}}_{ads}(T,\Xi=1) = \Delta G^{p_{std}}_{con}(T). \tag{11}$$

2.2 ALI^{c} extrapolation for temperatures above the critical temperature

Equation (6) is valid for the standard-molar-free-enthalpy of condensation $\Delta G^{p_{std}}_{con}(T)$ in the range $T \le T_{crit.}$. Experience shows that this function $\Delta G^{p_{std}}_{con}(T)$ corresponds to a straight line with very good approximation for almost all substances between the boiling temperature T_B at standard pressure and the critical temperature $T_{crit.}$, see Fig. 3,

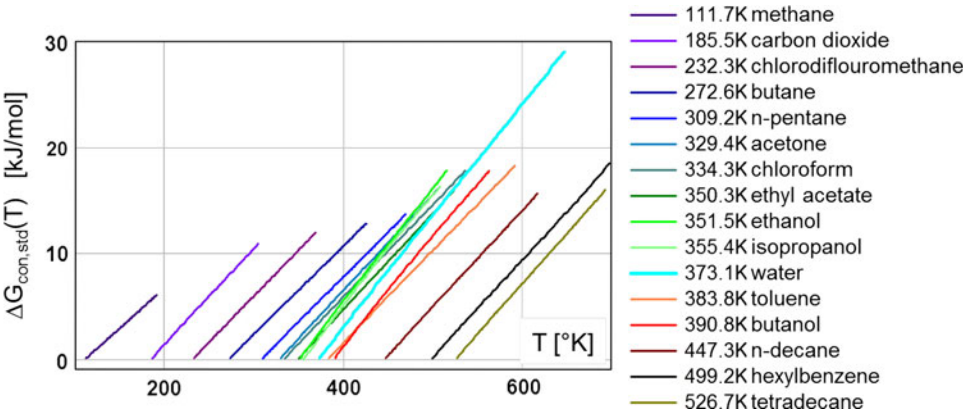


Fig. 3 Standard-molar-free-enthalpies of condensation $\Delta G^{p_{std}}_{con}(T)$ at standard pressure between boiling temperature and critical temperature as a function of temperature, a linear course exists for all 16 substances

containing property data from tables. The standard-molar-free-enthalpy of condensation $\Delta G^{p_{std}}_{con}(T)$ is no longer defined for $T > T_{crit.}$. Therefore, this function is extrapolated linearly for temperatures above the critical temperature $T_{crit.}$ using

$$\Delta G^{p_{std}}_{con}(T) = \frac{R\cdot T\cdot \ln\left(\frac{p_S(T_{crit.})}{p_{std}}\right)}{T_{crit.}-T_B}\cdot (T-T_B). \qquad (12)$$

Different extrapolation approaches for enthalpy of condensation are used in the literature (Nikolaev and Dubinin 1958; Cook and Basmadjin 1964; Seliverstova et al. 1986). Only measurements can verify whether or not our linear approach is justified. For temperatures above the critical temperature $T > T_{crit.}$, a hypothetical reference vapor pressure $p_S(T)$ of the pure adsorptive gas can be expressed as

$$p_S(T) = p_{std}\cdot e^{\left(\frac{\Delta G^{p_{std}}_{con}(T)}{R_m\cdot T}\right)}. \qquad (13)$$

2.3 The ALI^{c}-temperature-function

For the analytical description of the temperature dependence of the standard-molar-free-enthalpy of adsorption for the adsorbate-concentrate $\Delta G^{p_{std}}_{ads.Conc}(T,\Xi)$, a model concept was selected for the ALI^{c}-temperature-function in order to fulfill the following simple and obvious general conditions:

I. When the pores are completely filled $\Xi = 1$, the temperature dependence for the condensate $\Delta G^{p_{std}}_{ads.Conc}(T,\Xi = 1) = \Delta G^{p_{std}}_{con}(T)$ applies for the adsorbate.
II. At a negligible degree of pore filling $\Xi = 0$, temperature dependence is higher or lower by the factor $1 + K_T$. Then, K_T is used as a model parameter to fit the measured values.
III. At any standard temperature, $\Delta G^{p_{std}}_{ads.Conc}(T_{std},\Xi)$ has to merge into the temperature-independent function $\Delta G^{T_{std},p_{std}}_{ads.Conc}(\Xi)$.
IV. Interpolation is linear for intermediate degrees of pore filling, thus for $0 \le \Xi \le 1$.

With the above requirements, the ALI^{c}-temperature-function is expressed as

$$\begin{aligned}\Delta G^{p_{std}}_{ads.Conc}(T,\Xi) = {} & \Delta G^{T_{std},p_{std}}_{ads.Conc}(\Xi)\\ & + \left(\Delta G^{p_{std}}_{con}(T) - \Delta G^{T_{std},p_{std}}_{con}\right)\\ & \cdot (1 + (1-\Xi)\cdot K_T)\end{aligned} \qquad (14)$$

As for limiting cases of the ALI^{c}-temperature-function, a temperature-dependent constant is obtained at a negligible degree of pore filling $\Xi = 0$ and the molar-enthalpy of condensation is obtained when the pore is completely filled $\Xi = 1$. The ALI^{c}-temperature-function approaches the extrapolated value of $\Delta G^{p_{std}}_{con}(T)$ at $T > T_{crit.}$ and $\Xi = 1$. Obviously, other mathematical approaches are possible, for example those that cause a greater dependence on the degree of pore filling Ξ at low loading.

2.4 The ALI^{c}-pore-filling-function

A similar mathematical approach was selected, as the ALI^{c}-pore-filling-function, for the standard-free-enthalpy of adsorption at the standard pressure p_{std} and standard temperature T_{std} of the adsorbate-concentrate $\Delta G^{T_{std},p_{std}}_{ads.Conc}(\Xi)$ as was applied in (Schippert and Kimmerle 2008b). It also leads to thermodynamically consistent results for the limiting cases $\Xi = 0$ and $\Xi = 1$. In addition to the existing ALI exponential term for low loading and to the ALI linear term for loading values above this, see (Schippert and Kimmerle 2008b), two more terms were implemented:

- An exponential term for high degrees of pore filling. Presumably, it will only be of significance if a considerable number of mesopores are present in the

- adsorbent or, for example, for a combination of a very nonpolar with a very polar adsorbent.
- A Henry range at a finite degree of pore filling will only be of significance for very homogeneous pore size distribution and very low degrees of pore filling.

For the ALI^c-pore-filling-function $\Delta G^{T_{std},p_{std}}_{ads.Conc}(\Xi)$, the following is obtained:

$$\begin{aligned}\Delta G^{T_{std},p_{std}}_{ads.Conc}(\Xi) =&\left(\Delta G^{T_{std},p_{std}}_{ads.0.Conc} - \Delta G_{\exp.0}\right)\\ &+\Big(\Delta G^{T_{std},p_{std}}_{con} - \Delta G^{T_{std},p_{std}}_{ads.0,Conc} + \Delta G_{\exp.0}\\ &-\Delta G_{\exp.1}\Big)\Xi + \Delta G_{\exp.0}\cdot e^{\frac{-k_{G.\exp.0}\cdot\Xi}{(1-\Xi)}}\\ &+\Delta G_{\exp.1}\cdot e^{\frac{-k_{G.\exp.1}\cdot(1-\Xi)}{\Xi}} \qquad (15)\end{aligned}$$

2.4.1 *Limiting cases for the ALI^c-pore-filling-function at an arbitrary $T = T_{std}$*

A constant $\Delta G^{T_{std},p_{std}}_{ads.Conc}(\Xi = 0) = \Delta G^{T_{std},p_{std}}_{ads.0.Conc}$ is obtained at negligible pore filling $\Xi = 0$ and at standard temperature $T = T_{std}$ for the ALI^c-pore-filling-function, that is for the standard-molar-free-enthalpy of adsorption for the adsorbate-concentrate. A different value $\Delta G^{T_{std},p_{std}}_{ads.Conc}(\Xi = 1) = \Delta G^{T_{std},p_{std}}_{con}$ is obtained for each adsorptive gas when the pores are entirely filled $\Xi = 1$, see Fig. 4. For this reason, a simple and direct comparison of various adsorptive gas/adsorbent systems is not possible.

2.4.2 *Limiting cases of the ALI^c-pore-filling-function at $T = T_B$*

But if standard temperature is set to boiling temperature at standard pressure, the limiting cases $\Delta G^{T_B,p_{std}}_{ads.Conc}(\Xi = 1) = \Delta G^{T_B,p_{std}}_{con} = 0$ and $\Delta G^{T_B,p_{std}}_{ads.Conc}(\Xi = 0) = \Delta G^{T_B,p_{std}}_{ads.0.Conc} = \Delta G_{0AA}$ are obtained for the free-molar-enthalpy of the adsorption for the adsorbate-concentrate in which case the index $(0AA)$ means $(\Xi = 0, \text{Adsorptiv Gas}, \text{Adsorbens})$. The standard-molar-free-enthalpy of condensation $\Delta G^{T_B,p_{std}}_{con}$ at boiling temperature and when pores are completely filled disappears at the degree of pore filling $\Xi = 1$ for all systems, see Fig. 5. Hence a direct comparison of adsorptive gas/adsorbent systems is possible because all the adsorptive gas molecules are in a similar state, i.e. exactly in the state of vapour–liquid equilibrium at standard pressure. Therefore the values of the standard-molar-free-enthalpies of the adsorbate-concentrate ΔG_{0AA} at boiling temperature T_B and negligible degree of pore filling $\Xi = 0$ can be compared directly for different systems.

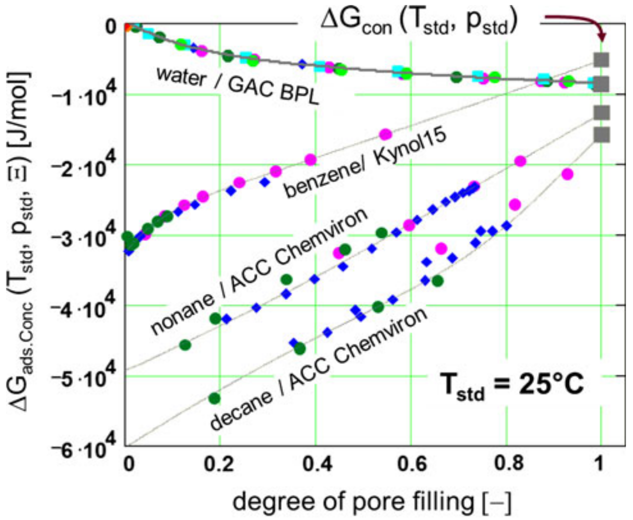


Fig. 4 Molar-free-enthalpies of adsorption for the adsorbate-concentrate at standard pressure and standard temperature 25 °C as a function of the degree of pore filling, the condensation value is reached in each case when the pores are entirely filled at $\Xi = 1$. The dots are measured values (Schippert 2003; Schippert et al. 2006; Rudisil Edgar et al. 1992), the lines have been fitted with the ALI^c-Model

2.5 Molar-free-enthalpy of adsorption

The complete and applicable ALI^c-equation for the molar-free-enthalpy of adsorption is obtained from Eq. (8) by introducing the ALI^c-temperature-function

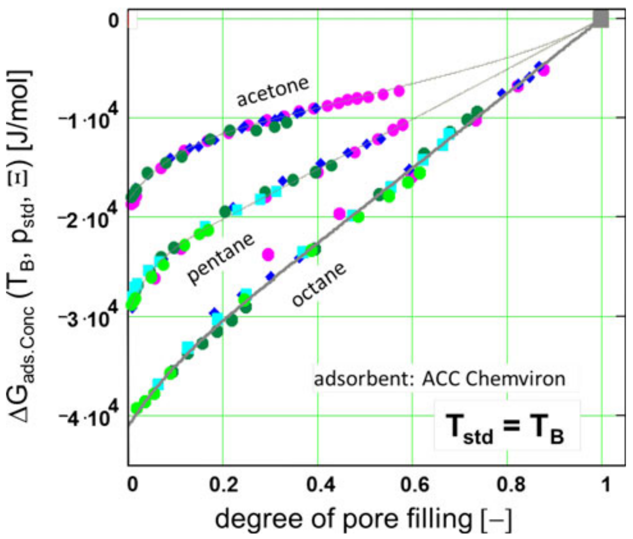


Fig. 5 Molar-free-enthalpies of adsorption at standard pressure and boiling temperatures of the adsorptive gases as a function of the degree of pore filling, all characteristic curves at $T = T_B$ run through one point, when the pores are entirely filled. The dots are measured values (Schippert 2003), the lines have been fitted with the ALI^c-Model

$$\Delta G^{p_{std}}_{ads}(T,\Xi) = \Delta G^{p_{std}}_{ads.mix}(T,\Xi) + \Delta G^{T_{std},p_{std}}_{ads.Conc}(\Xi) + \left(\Delta G^{p_{std}}_{con}(T) - \Delta G^{T_{std},p_{std}}_{con}\right) \cdot (1 + (1-\Xi)\cdot K_T). \tag{16}$$

With the ALI^c-pore-filling-function at standard reference temperature T_{std} it leads to

$$\begin{aligned}\Delta G^{p_{std}}_{ads}(T,\Xi) = {} & R\cdot T\cdot \ln\left(\Xi\cdot(1-\Xi)^{\frac{1-\Xi}{\Xi}}\right) \\ & + \left(\Delta G^{T_{std},p_{std}}_{ads.0,Conc} - \Delta G_{\exp.0}\right) \\ & + \left(\Delta G^{T_{std},p_{std}}_{con} - \Delta G^{T_{std},p_{std}}_{ads.0,Conc} + \Delta G_{\exp.0} - \Delta G_{\exp.1}\right)\Xi \\ & + \Delta G_{\exp.0}\cdot e^{\frac{-k_{G.\exp.0}\cdot\Xi}{(1-\Xi)}} + \Delta G_{\exp.1}\cdot e^{\frac{-k_{G.\exp.1}\cdot(1-\Xi)}{\Xi}} \\ & + \left(\Delta G^{p_{std}}_{con}(T) - \Delta G^{T_{std},p_{std}}_{con}\right)\cdot(1+(1-\Xi)\cdot K_T)\end{aligned} \tag{17}$$

Taking the boiling temperature T_B as the reference temperature, i.e. for each adsorptive the respective one, the above equation simplifies to:

$$\begin{aligned}\Delta G^{p_{std}}_{ads}(T_B,\Xi) = {} & R\cdot T_B\cdot \ln\left(\Xi\cdot(1-\Xi)^{\frac{1-\Xi}{\Xi}}\right) \\ & + \left(\Delta G_{0AA} - \Delta G_{\exp.0}\right) \\ & + \left(-\Delta G_{0AA} + \Delta G_{\exp.0} - \Delta G_{\exp.1}\right)\cdot\Xi \\ & + \Delta G_{\exp.0}\cdot e^{\frac{-k_{G.\exp.0}\cdot\Xi}{(1-\Xi)}} + \Delta G_{\exp.1}\cdot e^{\frac{-k_{G.\exp.1}\cdot(1-\Xi)}{\Xi}}\end{aligned} \tag{18}$$

At standard pressure with $\Delta G^{p_{std}}_{ads.mix}(T,\Xi=1)=0$ and $\Delta G^{p_{std}}_{ads.mix}(T,\Xi\to 0)\to -\infty$, the limiting cases for the adsorbate are obtained as $\Delta G^{p_{std}}_{ads}(T,\Xi=1) = \Delta G^{p_{std}}_{con}(T)$ and $\Delta G^{p_{std}}_{ads}(T,\Xi\to 0)\to -\infty$ for the standard-molar-free-enthalpy of adsorption. With this type of limit value behavior, the interaction between the adsorptive gas and the adsorbent cannot be investigated with respect to entropy and free enthalpy of adsorption. This is the reason, why only the adsorbate-concentrate may be considered for purposes of complete comparison.

2.6 The ALI^c isotherm equation explicit in p

In general terms, the ALI^c isotherm for the adsorbate is expressed explicitly in p as follows

$$p_{ALI^c}(T,\Xi) = p_{std}\cdot\left(\Xi\cdot(1-\Xi)^{\frac{1-\Xi}{\Xi}}\right)\cdot e^{\left(\frac{\Delta G^{p_{std}}_{ads.Conc}(T,\Xi)}{R_m\cdot T}\right)}. \tag{19}$$

The adsorbate-concentrate is described explicitly in p by

$$p_{ALI^c,Conc}(T,\Xi) = p_{std}\cdot e^{\left(\frac{\Delta G^{p_{std}}_{ads.Conc}(T,\Xi)}{R_m\cdot T}\right)}. \tag{20}$$

The relation of the ALI^c-temperature-function $\Delta G^{p_{std}}_{ads.Conc}(T,\Xi)$, which incorporates the ALI^c-pore-filling-function, has to be applied. The pressure relation of adsorbate and its concentrate is given by

$$\frac{p_{ALI^c}(T,\Xi)}{p_{ALI^c,Conc}(T,\Xi)} = \left(\Xi\cdot(1-\Xi)^{\frac{1-\Xi}{\Xi}}\right). \tag{21}$$

Using the measurement values $X_{excess,i}, p_i, T_i$ excess loading $X_{excess,i}$ is converted into the degree of pore filling Ξ_i required for the ALI^c-pore-filling-function by means of the relation $\Xi_i = \frac{X_{excessi}}{v_{ads}\cdot\left(\bar{\rho}_{as,T_{std}}\cdot e^{\beta_{as}\cdot(T_i-T_{std})} - \rho_{gas}(T_i,p_i)\right)}$. This is achieved at $p < 5$ bar and $T < T_{crit.}$ by $\Xi_i = \frac{X_{absi}}{X_{\max}(T_i)} = \frac{X_{absi}}{v_{ads}\cdot\left(\bar{\rho}_{as,T_{std}}\cdot e^{\beta_{as}\cdot(T_i-T_{std})}\right)}$ because $X_{abs\,i}\approx X_{excess\,i}$, otherwise absolute loading has to be converted into excess loading.

2.7 Model parameters

In addition to a first adjustable physical value $\Delta G^{T_{std},p_{std}}_{ads.0.Conc}$ or $\Delta G^{T_B,p_{std}}_{ads.0.Conc} = \Delta G_{0AA}$, a second fitting parameter K_T for temperature dependence is available to describe an adsorption system as well as two or four other fitting parameters, namely $\varDelta G_{\exp.0}$ with $k_{G\cdot\exp.0}$ and $\varDelta G_{\exp.1}$ with $k_{G\cdot\exp.1}$. The influence of these parameters on the functional course of the temperature-independent standard ALI^c-pore-filling-function can be seen in Fig. 6. Hence, the free-enthalpy of adsorption for the adsorbate-concentrate $\Delta G^{T_{std},p_{std}}_{ads.Conc}(\Xi)$ at standard pressure and standard temperature is described.

Similar to the ALI model (Schippert and Kimmerle 2008b), it is expected that the parameters $\Delta G_{\exp.1}$ with $k_{G\cdot\exp.1}$ are practically of no significance in adsorbents that are almost exclusively microporous. They only have an effect, when there is a considerable share of mesopores.

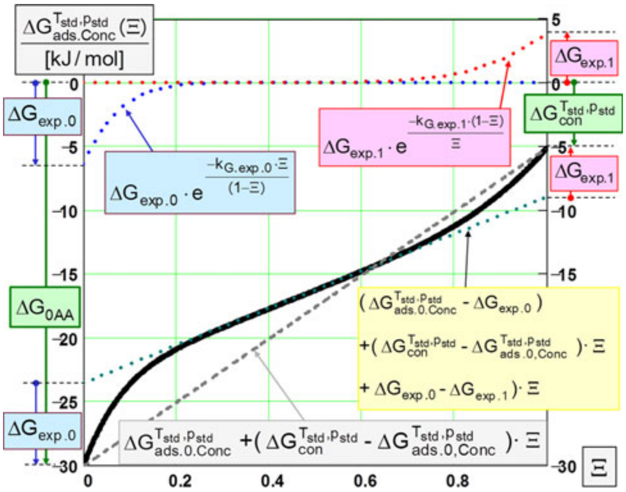


Fig. 6 Illustration of the influence of the fitting parameters $\varDelta G_{\exp.0}$ with $k_{G\cdot\exp.0}$ and $\varDelta G_{\exp.1}$ with $k_{G\cdot\exp.1}$ on the curve for the adjustment of the measured values in order to determine the molar-free-enthalpy of adsorption for the adsorbate-concentrate $\Delta G^{T_{std},p_{std}}_{ads.Conc}(\Xi=0) = \Delta G^{T_{std},p_{std}}_{ads.0.Conc}$ and $\Delta G^{T_{std},p_{std}}_{ads.Conc}(T_{std}=T_B,\Xi=0) = \Delta G_{0AA}$

Table 1 The table describes 20 adsorptive gas/adsorbent systems with *four* physical values and *five* fitting parameters, determined from measured values at boiling temperature and structured accordingly

Adsorbate	Adsorbent	Physical values				Parameters for measured value adjustment				
		V_{ads} [ml/100 g]	$\bar{\rho}_{as}$ [g/ml]	$\beta_{as} \times 10^3$ [1/K]	ΔG_{0AA} [J/mol]	K_T [−]	$\Delta G_{\exp.0}$ [J/mol]	$k_{G\cdot\exp.0}$ [−]	$\Delta G_{\exp.1}$ [J/mol]	$k_{G\cdot\exp.1}$ [−]
Methane	GAC CMS 55-2	38.7	0.35	−1.0	−10,621	0.127	−587	9.78	0	0
Methane	Porasil B	69.1	0.37	−2.8	−132	0.038	−3,075	3.03	0	0
n-Pentane	ACC Chemviron	55.5	0.54	−0.4	−30,061	0.367	−4,258	21.5	124	6.20
n-Hexane	ACC Chemviron	46.5	0.64	−0.5	−33,512	0.233	−3,076	13.3	1,643	3.09
Heptane	ACC Chemviron	49.4	0.59	0.0	−36,253	0.378	−3,128	6.60	4,105	2.90
n-Octane	ACC Chemviron	50.0	0.61	−0.8	−41,148	0.262	−3,316	10.9	0	0
n-Nonane	ACC Chemviron	53.3	0.61	−1.2	−45,774	−0.036	−3,959	10.1	723	2.39
n-Decane	ACC Chemviron	48.8	0.66	0.0	−45,621	−0.015	−3,000	10.0	4,825	2.18
Benzene	ACC Kynol 10	44.9	0.90	−2.1	−29,151	0.240	−2,229	23.8	377	10.22
Benzene	ACC Kynol 15	82.2	0.81	0.0	−25,428	0.453	−4,447	15.7	185	8.29
Toluene	ACC Chemviron	50.2	0.89	0.0	−31,513	0.280	−7,334	7.18	0	0
Ethyl acetate	ACC Kynol 15	65.7	0.83	0.0	−23,641	0.424	−4,387	13.8	5,067	5.87
Ethyl acetate	GAC Degussa WS IV	75.8	0.72	−1.9	−18,963	0.240	13,567	0.846	21	−1.24
Isopropanol	ACC Chemviron	48.4	0.58	−2.4	−22,609	0.049	−7,522	18.8	4,183	5.63
Acetone	ACC Chemviron	55.0	0.76	0.0	−19,351	0.108	−4,793	11.8	1,814	8.39
Dichloro-methane	ACC Kynol 15	88.0	1.27	0.0	−14,871	0.316	−3,208	17.6	0	0
H_2O	GAC BPL	42.1	0.91	−0.3	11,234	0.262	3,591	9.19	2,078	2.04
CO_2	GAC CMS 55-2	34.0	1.26	−1.8	−7,875	0.044	−906	7.15	0	0
CO_2	ACC Chemviron	51.0	1.31	−2.4	−5,367	−0.039	−1,346	5.67	0	0
CO_2	GAC F400	59.2	1.17	−2.8	−4,482	−0.022	−2,637	0.568	1,500	0.29

Physical values 1–4: 1. specific accessible adsorption volume v_{ads} [ml/100 g], 2. mean density of the adsorbate $\bar{\rho}_{as}(T, \Xi)$ [g/ml], 3. thermal coefficient of expansion β_{as} [1/K] of the adsorbate, 4. molar characteristic zero value of adsorption ΔG_{0AA} [J/mol]

Fitting parameters 1–5: 1.&2. Linear parameters, $\Delta G_{\exp.0}$, $\Delta G_{\exp.1}$ [J/mol], 3.&4. exponential parameters $k_{G\cdot\exp.0}$, $k_{G\cdot\exp.1}$ [−], 5. parameter for temperature adjustment K_T [−]

Therefore, depending on the system, 3 or 5 pure fitting parameters are adequate in most cases to describe the adsorption system in question, while the Henry range has to be dealt with separately only in a few cases known.

The values for the greatest accessible specific adsorption volume v_{ads}, the mean density of the adsorbate $\bar{\rho}_{as}(T, \Xi)$ and the thermal expansion coefficient β_{as} can be predefined, if already known, or also be determined by the fitting process. The four physical values v_{ads}, $\bar{\rho}_{as}$, β_{as}, ΔG_{0AA} and the five fitting parameters K_T, $\Delta G_{\exp.0}$, with $k_{G\cdot\exp.0}$, $\Delta G_{\exp.1}$ with $k_{G\cdot\exp.1}$ are determined for 20 isotherm fields measured by applying a multi-stage fitting process which reliably prevents local minima and minimizes the number of fitting parameters, see Table 1.

For example, it is to be expected that:

- physical and thermodynamic conclusions regarding the type and strength of bonding for the adsorptive gas as a function of pore size distribution can be made by considering the parameters ΔG_{0AA} and $\Delta G_{\exp.0}$ with $k_{G\cdot\exp.0}$, which determine the degree of pore filling between 0 and 0.9.
- the amount for ΔG_{0AA} increases as the chain length of the alkanes increases,
- the amount for $\Delta G_{\exp.0}$ decreases as the chain length of the VOCs increases,
- the influence of $\Delta G_{\exp.0}$ decreases as the average pore diameter increases,
- linear molecules have a considerably greater ΔG_{0AA} compared to highly branched isomers (e.g. pentane/tetramethyl-ethane and *n*-butylbenzene/*tert*-butylbenzene) and
- more information regarding the influence of heterocyclic atoms and heterocyclic atom groups such as OH, F, Cl, O–C=0 can be obtained.

3 The application of the ALI^c-Model

At this point, examples of adsorptive gas/adsorbent systems will be used to verify that the ALI^c-Model can be applied to describe isotherm fields measured in extensive pressure and temperature ranges. The commercial

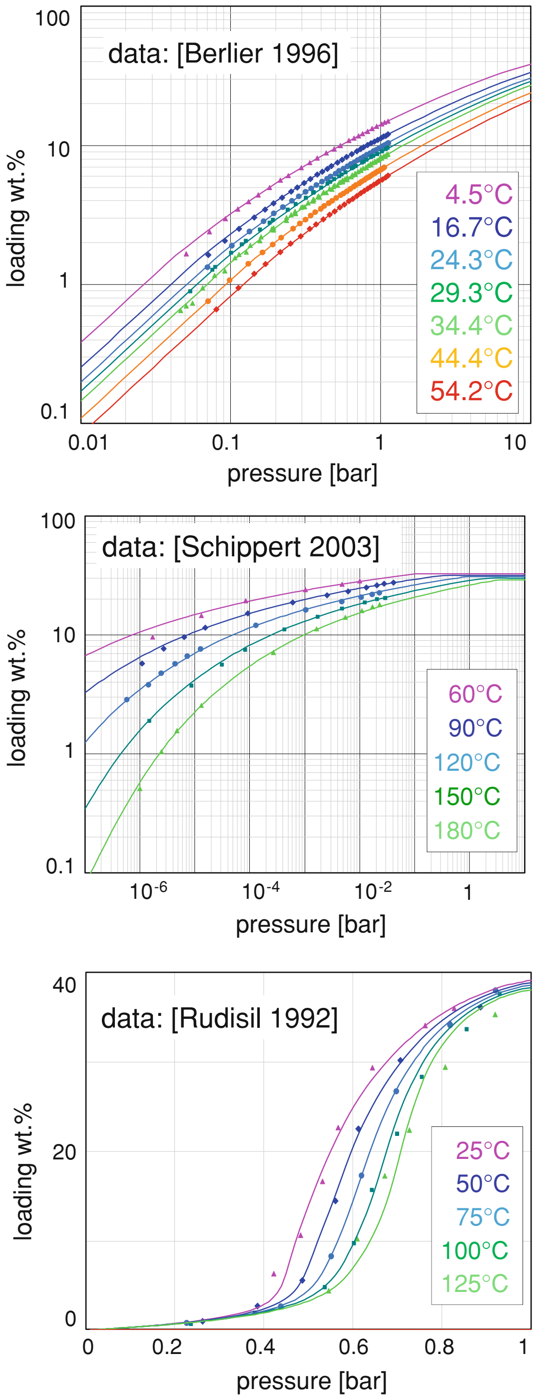


Fig. 7 Measurements in the low pressure range of the adsorption isotherms for carbon dioxide on ACC Chemviron, $T_B \sim -88$ °C (top), for octane on ACC Chemviron, $T_B \sim 125$ °C (centre) and for water on GAC BPL, $T_B \sim 100$ °C (bottom). The dots are measured values; the lines have been fitted with the ALI^c-Model

adsorbents all are microporous or microporous/mesoporous that are

- ACC: Chemviron FM5/250, Kynol 5092-10/15,
- GAC: type BPL, CMS 55-2, Degussa WSIV, F400,
- Silica gel: Porasil B and

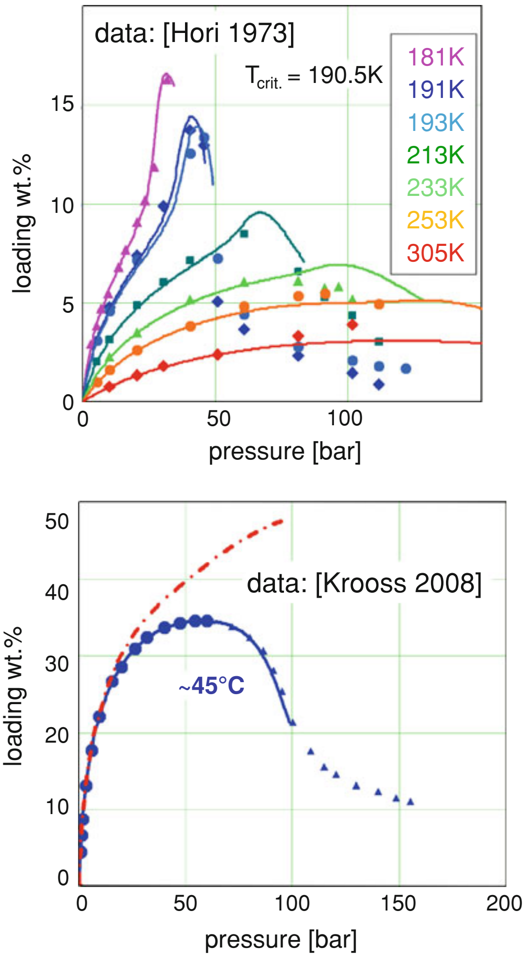


Fig. 8 Measurements in the high pressure range of the adsorption isotherms for methane on Porasil (Hori and Kobayashi 1973) (top) at the temperatures 181, 191, 193, 213, 233, 253 and 305 K, the critical temperature is 190.6 K. Measurements of the adsorption isotherms for carbon dioxide on F400 activated carbon at the supercritical temperature of 318 K (Krooss et al. 2009) (bottom), red the absolute and blue excess values of loading. The curves were calculated by using only the blue round points to show the extrapolation ability of the ALI^c-Model

- Zeolite: 5A.

All cited data are listed as Electronic Supplementary Material. Access: http://www.htw-saarland.de/forschung/struktur/forschungseinrichtungen/ipp.

3.1 Solvents, gas and water on activated carbon at low pressure

Figure 7 shows the measurements of the adsorption isotherms for gas, solvents and water on activated carbon in the low pressure range. The carbon dioxide, $T_B \sim -88$ °C, on ACC Chemviron type FM5/250 (Berlier and Frere 1996), 10^{-3} to 10 bar can be seen in the upper part of the figure while high-boiling octane, $T_B \sim +125$ °C, on

ACC Chemviron type FM5/250 (Schippert 2003), 10^{-6} to 10 bar is in the center and water $T_B \sim +100$ °C, on GAC type BPL (Rudisil Edgar et al. 1992), 0.1–1 bar is in the lower region.

3.2 Gases on Porasil and activated carbon at high pressure

The curves in the upper section of Fig. 8 were determined from measurements of methane on Porasil (Hori and Kobayashi 1973) as an example using the ALI^c-Model. The dots are the values measured at the temperatures 181, 191, 193, 213, 233, 253 and 305 K. In this case, it should be noted that the critical temperature for methane is $T_{crit} = 190.6$ K and thus it is the highest (purple) curve below the critical temperature while the other four curves are above it.

The values of an isotherm field for carbon dioxide on F400 activated carbon were measured at 45 °C by three different institutes, TU-Delft, TU-Mons and RWTH Aachen and presented in the report (Krooss et al. 2009). The measurements are shown in the lower section of Fig. 8. The relevant curves, that are blue for excess loading and red for total loading, were determined. In order to prove the extrapolation capability of the ALI^c-Model, only the blue measurement points up to roughly 60 bar were used for fitting and the curve up to a pressure of 100 bar was extrapolated.

In each case, the ALI^c-Model worked correctly to the end of the solid line. Beyond these pressures, the density of the adsorbate started to influence results considerably. At very high pressures the density function of the adsorbate is pressure-dependent and currently not yet implemented and covered by the model.

3.3 ALI^c analysis of adsorptive gas/adsorbent systems

3.3.1 *Characteristic curves at* $T = T_B$

In accordance with the ALI^c-Model concept, $\Delta G^{T_B,p_{std}}_{ads.Conc}(\Xi = 1) = 0$ is obtained for the free-enthalpy of adsorption for the adsorbate-concentrate when pores are filled. The characteristic-zero-value of the adsorption system $\Delta G^{T_B,p_{std}}_{ads.Conc}(\Xi = 0) = \Delta G_{0AA}$ is obtained for unfilled pores. Consequently, the characteristic-curve for adsorption is calculated for each system as a unique shape of curve by

$$\Delta G^{T_B,p_{std}}_{ads.Conc}(\Xi) = R \cdot T_B \cdot \ln\left(\frac{p(T_B,\Xi)}{p_{std}}\right) - R \cdot T_B \cdot \ln\left(\Xi \cdot (1-\Xi)^{\frac{1-\Xi}{\Xi}}\right) \tag{22}$$

The function of the free-enthalpy of adsorption for the adsorbate-concentrate at standard pressure p_{std} and boiling temperature T_B is a tool for comparing the adsorptive gas/adsorbent systems. The characteristic-curves of adsorption for 16 different adsorptive gas/adsorbent systems are shown in Fig. 9. Some measurement points for three isotherm measurements for water on granular activated carbon (GAC BPL), methane on silica gel (Porasil B) and benzene on activated carbon fiber cloth (ACC Kynol type 5092-15) are also plotted. The different colors for the measured points represent different test temperatures. The orange, red and pink lines represent the group of alkanes on activated carbon fiber cloths.

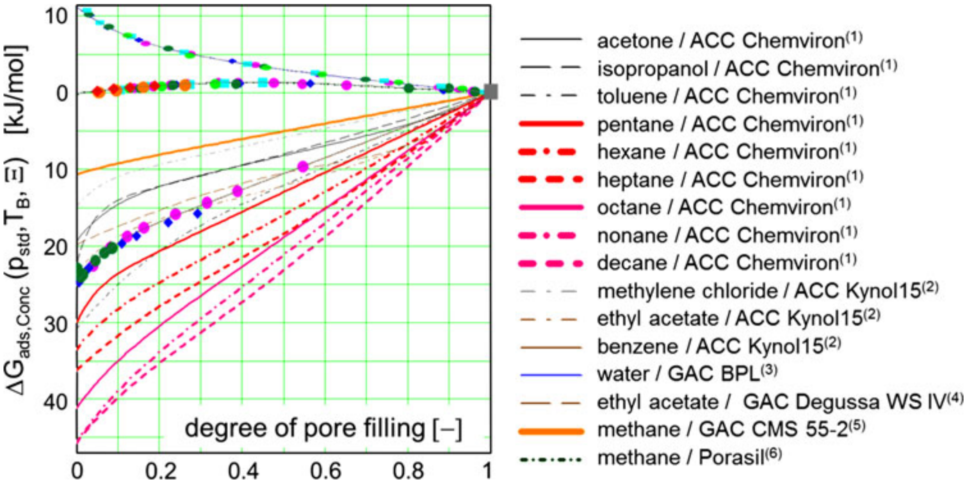


Fig. 9 Characteristic adsorption curves of various adsorptive gas/adsorbent systems, some measured points for three isotherms are shown as an example, water/GAC BPL, methane/Porasil and benzene/ACC Kynol 15. The different colors represent different test temperatures. The group of alkanes on activated carbon fiber cloth are highlighted in orange, red and pink. The dots are measured values ([1]Schippert 2003, [2]Schippert et al. 2006, [3]Rudisil Edgar et al. 1992, [4]Mersmann 1999, [5]Berlier and Frere 1996, [6]Hori and Kobayashi 1973), the lines have been fitted with the ALI^c-Model

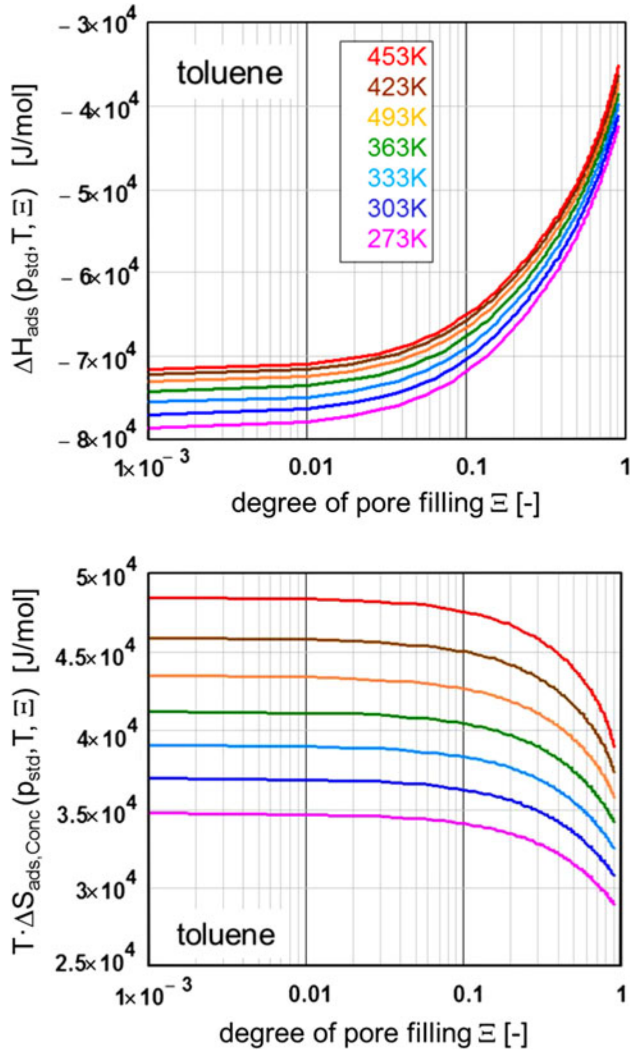


Fig. 10 The courses of the molar-enthalpy of adsorption for adsorbate and adsorbate-concentrate (top) and the product of temperature multiplied by the molar-entropy of adsorption for the adsorbate-concentrate (bottom) for the system toluene on ACC Chemviron (Schippert 2003) as a function of the degree of pore filling and temperature at standard pressure in each case. Both functions have finite values at negligible pore filling

3.3.2 Molar-enthalpy and -entropy of adsorption

The fitting function of the ALI^c-Model obtained from measured values allows the isochoric-molar-enthalpy $\Delta H_{ads}^{isochor}(T,\Xi)$ of adsorption at a constant degree of pore filling Ξ to be calculated as

$$\Delta H_{ads}^{isochor}(T,\Xi) = R\cdot\left(\frac{d\ln\left(\frac{p_{ALI^C}(T,\Xi)}{p_{std}}\right)}{d(1/T)}\right)_{\Xi} \cdot\left[Z(T,p(T,\Xi)) - \left(\frac{p_{ALI^C}(T,\Xi)}{R\cdot T}\right)\cdot\frac{MW}{\rho_{ads.mean}(T,\Xi)}\right] \tag{23}$$

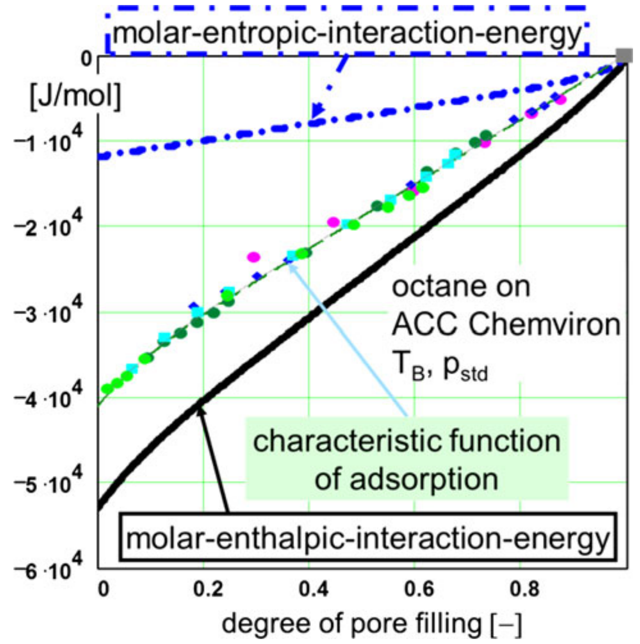


Fig. 11 For the system octane on ACC Chemviron (Schippert 2003) at boiling temperature and standard pressure, the courses of the molar-free-enthalpy of adsorption (with dots of measured values), the molar-enthalpy of adsorption for the adsorbate or the adsorbate-concentrate (black) and the product from boiling temperature multiplied by the molar-entropy of adsorption for the adsorbate-concentrate (blue) are shown as a function of the degree of pore filling. The new definitions for these functions are specified in the figure

Since an athermal mixture is assumed, $\Delta H_{ads}^{isochor}(T,\Xi) = \Delta H_{ads.Conc}^{isochor}(T,\Xi)$ applies for the molar-enthalpy of adsorption for the adsorbate and the molar-enthalpy of adsorption for the adsorbed adsorbate-concentrate. The real gas corrections $Z(T,p(T,\Xi))$ have to be taken into account in this case for pressures above 1 bar. Using the adsorption enthalpy $\Delta H_{ads}^{isochor}(T,\Xi)$ determined in this way, the standard-molar-entropy of adsorption for the adsorbate-concentrate $\Delta S_{ads.Conc}^{p_{std}}(T,\Xi)$ from $\Delta G_{ads.Conc}^{p_{std}}(T,\Xi)$ can be calculated as follows

$$\Delta S_{ads.Conc}^{p_{std}}(T,\Xi) = \frac{\Delta H_{ads}^{isochor}(T,\Xi) - \Delta G_{ads.Conc}^{p_{std}}(T,\Xi)}{T} \tag{24}$$

Both, the thermodynamic ALI^c functions $\Delta H_{ads}^{isochor}(T,\Xi)$ and $\Delta S_{ads.Conc}^{p_{std}}(T,\Xi)$ are intended to provide information on the strength and type of bonding for the adsorbate-concentrate on the pore wall and the structure inside the adsorbate, respectively. For this reason in Fig. 10, the isochoric molar-enthalpy of adsorption $\Delta H_{ads}^{isochor}(T,\Xi)$ for the adsorbate or the adsorbate-concentrate (top) and the product of temperature multiplied by the standard-entropy of adsorption for the adsorbate-concentrate $T\cdot\Delta S_{ads.Conc}^{p_{std}}(T,\Xi)$ (bottom) is presented in logarithmic form as a function of

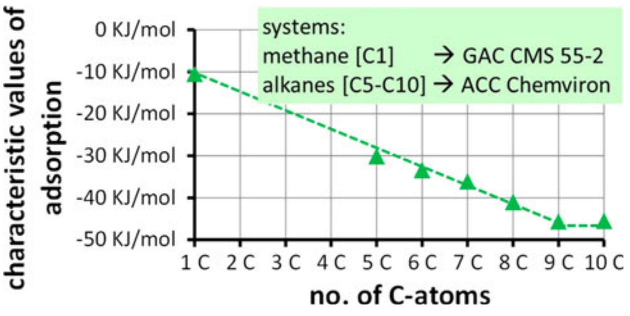


Fig. 12 Characteristic values, i.e. the molar-free-enthalpies of adsorption for the adsorbate-concentrate at negligible degree of pore filling $\Xi = 0$ at boiling temperature and standard pressure as a function of the number of carbon atoms of its chemical formula in each case

the degree of pore filling and the temperature for toluene. It can be easily seen that both functions have finite values at negligible pore filling.

It is also interesting to compare the trends of the standard-molar-enthalpy of adsorption for the adsorbate or the adsorbate-concentrate and the standard-molar-entropy of adsorption for the adsorbate-concentrate with the values for the pure condensed phase of the adsorptive gas. The relation applies

$$\Delta G^{T_B,p_{std}}_{ads.Conc}(\Xi) = \Delta H^{isochor}_{ads}(T_B,\Xi) - T \cdot \Delta S^{p_{std}}_{ads.Conc}(T_B,\Xi) \tag{25}$$

which is illustrated in Fig. 11 for octane. The trends of the pure bonding term of the adsorption energies of the condensed phase can be shown as a function of the degree of pore filling by the differences $\Delta H^{isochor}_{ads}(T_B,\Xi)$ $-\Delta H^{p_{std}}_{con}(T_B)$ of the molar-enthalpic-interaction-energy (black, solid) and $T_B \cdot \Delta S^{p_{std}}_{ads.Conc}(T_B,\Xi) - T_B \cdot \Delta S^{p_{std}}_{con}(T_B)$ of the molar-entropic-interaction-energy (blue, dotted).

3.3.3 *Limit values at negligible pore filling $\Xi = 0$*

At standard pressure p_{std}, boiling temperature T_B and negligible degree of pore filling $\Xi = 0$, the following four thermodynamic values are finite:

- molar-characteristic-zero-value of adsorption $\Delta G^{T_B,p_{std}}_{ads.Conc}(\Xi = 0) = \Delta G_{0AA}$
- molar-enthalpic-zero-energy of adsorption $\Delta H^{isochor}_{ads}(T_B,\Xi = 0) - \Delta H^{p_{std}}_{con}(T_B)$
- molar-entropic-zero-energy of adsorption $T_B \cdot \left[\Delta S^{p_{std}}_{ads.Conc}(T_B,\Xi = 0) - \Delta S^{p_{std}}_{con}(T_B)\right]$
- molar-zero-entropy of adsorption $\Delta S^{p_{std}}_{ads.Conc}(T_B,\Xi = 0) - \Delta S^{p_{std}}_{con}(T_B)$

These four values can be useful for the development and assessment of adsorbents designed for special separation purposes.

3.3.4 *Alkanes on ACC Chemviron at T_B and $\Xi = 0$*

Figure 12 shows the molar-characteristic-zero-values of adsorption for alkanes, methane, pentane, hexane, heptane, octane, nonane and decane as a function of the number of their carbon atoms. In each case, it is the standard-molar-free-enthalpy of adsorption for the adsorbate-concentrate at negligible degree of pore filling $\Xi = 0$ and at boiling

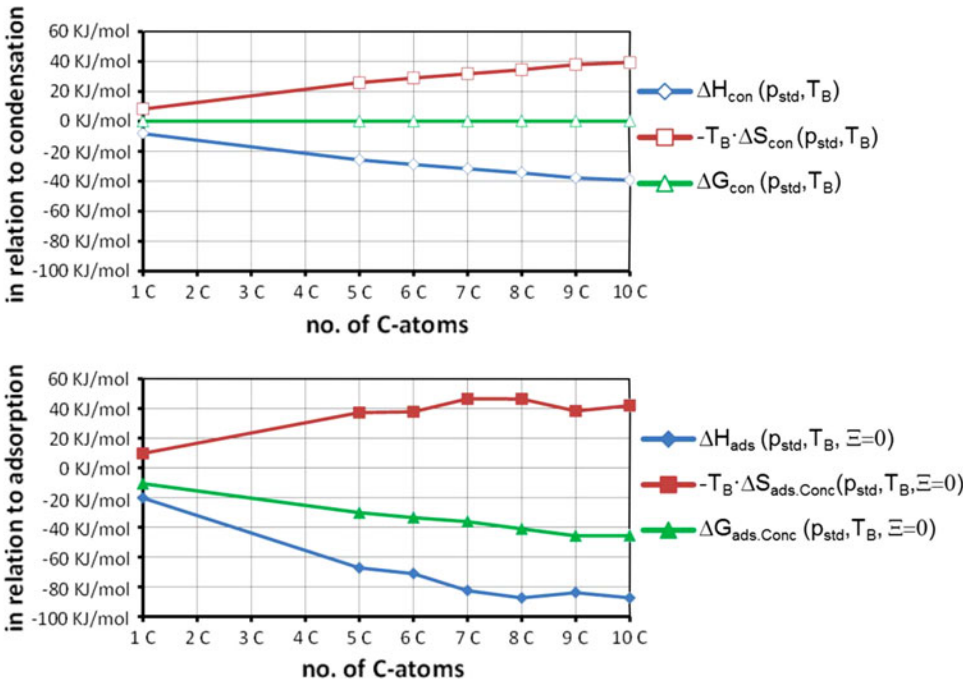
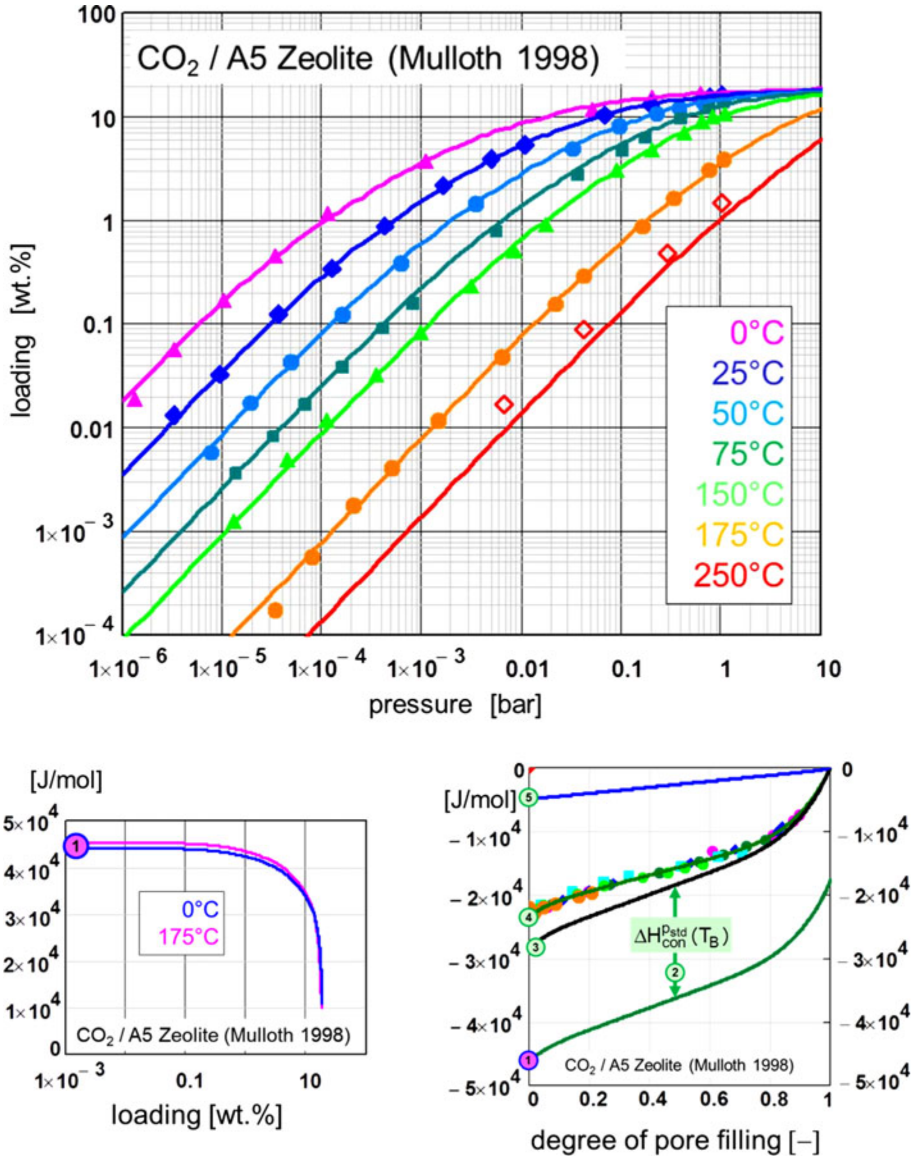


Fig. 13 The molar-enthalpies, the negative products of boiling temperatures multiplied by the molar-entropies and the free-molar-enthalpies for condensation of the adsorptive gas (upper section) and for adsorption of the adsorbate-concentrate (lower section) at negligible degree of pore filling $\Xi = 0$, at standard pressure and boiling temperature as a function of the number of carbon atoms. The difference is caused by binding forces

Fig. 14 Adsorption-isotherms of carbon dioxide on 5A Zeolite (Mulloth and Finn 1998) (top), point 1 (bottom left and right) is the isochore/isostere adsorption-enthalpy and marked by point 2 (bottom right) is the molar-enthalpy of condensation. Point 3 is the molar-enthalpy of adsorption for adsorbate and for adsorbate-concentrate. Point 4 is the molar-free-enthalpy of adsorption for the adsorbate-concentrate and point 5 the boiling temperature multiplied by the molar-entropy of adsorption for the adsorbat-concentrate. The courses illustrate the dependencies of pore filling



temperature. Unfortunately, the qualities of the measurements at negligible degree of pore filling, which are presented in this study, vary because they were not conducted specifically for this purpose. Therefore, the results should be considered as tendencies.

As for the alkanes, the comparative values of the molar-enthalpy of condensation (blue unfilled rhombuses), of the negative product from boiling temperature multiplied by molar-entropy (red unfilled rectangles) and of the molar-free-enthalpies (green unfilled triangles) at standard pressure and boiling temperature are presented in the upper section of Fig. 13. It can be seen that the standard-free-molar-enthalpies for condensation always become the value of zero, in accordance with the expression $\Delta H^{p_{std}}_{con}(T_B) - T_B \cdot \Delta S^{p_{std}}_{con}(T_B) = 0$.

The lower section of Fig. 13 shows, for the alkanes, the values of the molar-enthalpy of adsorption (blue filled rhombuses), of the negative product from boiling temperature multiplied by the molar-entropy (red filled rectangles) and of the molar-free-enthalpy of adsorption (green filled triangles) for the adsorbed concentrate at standard pressure, boiling temperature and negligible degree of pore filling $\Xi = 0$. By

Table 2 Description of characteristic values for Fig. 14

Point no.	Equation	Values of CO$_2$ on Zeolite 5A (kJ/mol)
1	$\Delta H^{isochor}_{ads}(T_B, \Xi = 0)$	−46.2
2	$\Delta H^{p_{std}}_{con}(T_B)$	−17.8
3	$\Delta H^{isochor}_{ads}(T_B, \Xi = 0) - \Delta H^{p_{std}}_{con}(T_B)$	−28.4
4	$\Delta G^{T_B, p_{std}}_{ads.Conc}(\Xi = 0) = \Delta G_{0AA}$	−23.4
5	$T_B \cdot \left[\Delta S^{p_{std}}_{ads.Conc}(T_B, \Xi = 0) - \Delta S^{p_{std}}_{con}(T_B)\right]$	−5.0

comparing the upper and lower sections, it can be seen how the adsorption process affects the values. This illustration allows condensation and adsorption to be compared.

3.3.5 Analysis of system carbon dioxide on 5A Zeolite

In Mulloth and Finn (1998), the Tóth model (Tóth and József 2002) is used to describe adsorption isotherms of carbon dioxide on Zeolite 5A with 21 parameters for 7 temperatures from 25 to 250 °C and pressures between 0 and 1 bar. The relative error runs from 2 to ~9 % and the values of the 21 parameters allow no physical interpretation. The isosteric heat of adsorption was calculated to 44.9 kJ/kg, see also (Ruthven et al. 1973, 45.2 kJ/kg). The ALI^c-Model with only 5 adjusting parameters demonstrates that the measured values at 250 °C are questionable, see Fig. 14. Then, the updated adsorption isotherms exhibit a relative error of only ~5.8 %. Bottom left diagram shows the temperature dependent isosteric adsorption-enthalpy of adsorption at 0 und 175 °C as a function of loading, drawn in analogy to Mulloth and Finn (1998). In the bottom right diagram, the characteristic ALI^c-Model values of Table 2 can be read out as distances between points. Molar isosteric and isochore adsorption-enthalpy of adsorption cannot be distinguished because of measurement inaccuracy, but are shown as point 1 in Fig. 14 (bottom left and right). Subtracting the molar-enthalpy of condensation point 2, it results the molar-enthalpy of adsorption for adsorbate and adsorbate-concentrate point 3. If point 5, the molar-entropic-zero-energy of the adsorbate-concentrate is subtracted, the molar-characteristic-zero-value of adsorption results, that is point 4, the molar-free-enthalpy of adsorption for the adsorbate-concentrate. The molar-zero-entropy of adsorption for adsorbate-concentrate $\Delta S^{p_{std}}_{ads.Conc}(T_B, \Xi = 0) - \Delta S^{p_{std}}_{con}(T_B) = -0.96$ kJ/(mol K) cannot be shown here.

4 Summary

The ALI^c-Model describes adsorption-isotherm-fields of adsorptive gas/adsorbent systems in one equation by four to nine parameters with physical meaning. So far, all technical applications in terms of temperature, pressure and materials could be handled. Because of its thermodynamic basis, the ALI^c-Model allows a safe interpolation and extrapolation when significant measurements at different temperatures and pressures are available. Even an extrapolation from a known to an unknown system should work. By using the group of alkanes on activated carbon as an example, measurements indicate that the characteristic zero value of adsorption is a linear function of the number of carbon atoms, up to 9 carbon atoms.

The ALI^c-Model allows a thermodynamic comparison of the systems via three characteristic curves: free-enthalpy, enthalpy and entropy of adsorption. In addition, at a negligible degree of pore filling, it provides four characteristic adsorption values, namely the characteristic-zero-value, the enthalpic-zero-energy, the entropic-zero-energy and the zero-entropy of adsorption for the thermodynamic analysis of the interaction of adsorbent and adsorbate-concentrate.

Comparing for instance the courses of the molar-free-enthalpy, the molar-enthalpy and the product of boiling temperature multiplied by the molar-entropy of adsorption and the molar-enthalpy of condensation it is obvious, how intuitive the thermodynamics of adsorption can be illustrated by the ALI^c-Model.

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