Adsorption (2009) 15: 337–353
DOI 10.1007/s10450-009-9189-2

# Water isotherm models for 4A (NaA) zeolite

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Received: 1 October 2007 / Accepted: 13 May 2009 / Published online: 29 May 2009

**Abstract** The adsorption data of Gorbach et al. (Adsorption 10(1): 29–46, 2004) and Morris (J. Colloid Interface Sci. 28: 149–155, 1968) for the adsorption of water on 4A zeolite pellets is re-analyzed. Model isotherms are derived considering a two site hypothesis, one for the $\alpha$ cage and one for the $\beta$ cage. Four simple model isotherms are fitted to the data. Both a dual site Toth or dual site Langmuir isotherm model fit the data adequately.

The optimized standard enthalpy and entropy of adsorption parameters derived from the data are surprising for the $\beta$ cage. The optimized standard enthalpy of the $\beta$ cage is 1/3rd of that observed calorimetrically, and the standard entropy of adsorption is positive, a physical impossibility. Substituting the calorimetric enthalpy of adsorption corrected the standard differential entropy of sorption values resulting in the standard entropy of sorption values varying significantly with temperature. This variation is postulated to be due to either water of hydration formation, or clathrate formation, or the formation of clusters of water such as dimers, trimers, etc.

**Keywords** Adsorption · Water · 4A (NaA) zeolite · Langmuir isotherm · Toth isotherm · Ruthven isotherm · Dual site isotherm · Standard enthalpy of adsorption · Standard entropy of adsorption

## Nomenclature

| | |
|---|---|
| $f_i$ | fractional size of site $i$ |
| $K_{ci}$ | dimensionless equilibrium constant $ci$, $c\beta$ for cage $\beta$ and $c\alpha$ for cage $\alpha$ respectively |
| $K_i$ | equilibrium parameter $i$, 1 for cage $\beta$ and 2 for cage $\alpha$ respectively, mbar$^1$ |
| $H_i$ | Henry constants, for cages $\beta$ and $\alpha$ respectively, g/g.mbar |
| $H_{oi}$ | pre-exponential Henry parameter, g/g.mbar |
| $m_{\max}$ | maximum number of terms in Ruthven model, $\equiv v/\beta_H$ |
| $m_i$ | Toth equilibrium parameter, for cages $\beta$ and $\alpha$ respectively, units |
| $MW_{\mathrm{H_2O}}$ | molecular weight of water |
| $n$ | number of data points in regression calculations |
| $n_{\max}$ | maximum molecules of water puc |
| $N_o$ | Avogadro's number |
| $p$ | pressure, mbar |
| $q$ | adsorbed phase concentration, g/g |
| $q_{\mathrm{sat}}$ | saturated adsorbed phase concentration, g/g |
| $q_{\mathrm{sat\ crystal}}$ | saturated adsorbed phase concentration for pure 5A crystals, g/g |
| $R$ | gas constant, kJ/mol.K |
| $t_i$ | toth heterogeneity parameter, dimensionless |
| $T$ | temperature, K |
| $T_C$ | critical temperature, K |
| $V_\beta$ | volume of $\beta$ cage, Å$^3$ |
| $V_\alpha$ or $v$ | volume of $\alpha$ cage, Å$^3$ |
| $V_{\mathrm{cell}}$ | volume of pseudo unit cell of 5A, 1870 Å$^3$ |
| $y_{i,\mathrm{exp}}$ | experimental data point, g/g |
| $y_{i,th}$ | theoretical data point, g/g |
| Z | zeolite |

## Greek letters

| | |
|---|---|
| $\alpha$ | cage $\alpha$ |
| $\beta$ | cage $\beta$ |
| $\beta_H$ | molecular volume of water molecule, Å$^3$ |
| $(-\Delta H)$ | heat of adsorption, kJ/mole |
| $(-\Delta H^0)$ | standard heat of adsorption, kJ/mole |

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| | |
|---|---|
| $\Delta S$ | standard entropy of sorption, kJ/mole.K |
| $\rho$ | density of dehydrated crystal lattice, g/cc |
| $\omega$ | fractional weight of crystals in pellet, dimensionless |
| $\theta_i$ | fractional loading |

## 1 Introduction

The sorption of water on 4A zeolite exhibits bifurcation behavior. This is due to the availability of two cavities in the pseudo unit cell, the $\alpha$ and $\beta$ cages respectively, each of which is accessible to water. As the size ratio of these cavities is approximately 5 to 1 the adsorption behavior is expected to vary significantly in each cavity.

A summary of the principal literature aspects needed for this work is provided in Table 1. Breck's (1974) book provides details on the 4A zeolite physical characteristics. The pseudo cell formula is given on the 1st line in Table 1, and Breck indicates that the Si/Al ratio may vary from 0.7 to 1.2 with possible occlusion of $NaAlO_2$ in the $\beta$ cages. He provides a dehydrated density of 1.99 g/cc, a unit cell volume of 1870 Å$^3$, a $\beta$ cage volume of 151 Å$^3$, and an $\alpha$ cage volume of 775 Å$^3$ giving a total pore volume of 926 Å$^3$ and a specific volume of 320 cc/kg.

The saturation loading of water on the 4A zeolite crystals is given by Breck as 0.28 or 0.285 g/g Z and by Ulku et al.

**Table 1** Pertinent literature data for water adsorption on 4A zeolite

| Typical pseudo cell unit contents | | $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}].27H_2O$ | |
|---|---|---|---|
| Crystallographic data | | | |
| Cubic, dimensions | | 12.32 Å | |
| Pseudo unit cell volume | | 1870 Å$^3$ | |
| Density | | 1.99 g/cc | |
| Void volume | | 0.47 cc/cc | |
| Aperture size | | 2.2 Å$\beta$ cage, 4.2 Å$\alpha$ cage | |
| Volume $\beta$ cage, $V_\beta$ | | 151 Å$^3$ | |
| Volume $\alpha$ cage, $V_\alpha$ | | 775 Å$^3$ | |
| Pore volume, $V_P$ (calc.) | | 926 Å$^3$ puc, 320 cc/kg | |
| Saturated loadings | | | |
| 4A crystals | | 0.28, 0.285 g/g Breck | |
| 4A crystals | | 0.265 g/g Ulku et al. | |
| Linde 4A pellets | | ≈0.20 g/g Breck | |
| Linde 4A pellets | | ≈0.20 g/g Morris | |
| Linde 4A pellets | | ≈0.2058 g/g Jury and Horng | |
| Davison 4A pellets | | ≈0.20 g/g Gorbach et al. | |
| Heats of adsorption, kJ/mol | $\Theta$ low | $\Theta$ high | Author |
| | 125.5 | 74.06 | Breck |
| | 101.7 | 62.76 | Dubinin et al. |
| | 104.6 | decreasing | Vergnaud et al. |
| | 100 | <60 | Zhdanov et al. |
| | 47.78 | 19.98 | Ulku et al. |
| | | 62.76 | Avgul et al. |
| | | 62.43 | Jury and Horng |
| | | | Cointot et al. |
| Isotherm models | | | |
| | Langmuir | Cui; Carter & Husain; Ulku et al. | |
| | Two site Langmuir | Jury and Horng | |
| | Polanyi Potential Theory | Cointot et al., Qin | |
| | Dubinin | Cointot et al. | |
| | 18 models | Gorbach et al. | |

All data not annotated is from Breck's book

(2005) as 0.265 g/g Z. For the Linde and Davison 4A pellets which consist of 80% zeolite crystals, the saturation loading is approximately 0.2 (Breck 1974; Morris 1968; Gorbach et al. 2004) and 0.2058 g/g pellet (Jury and Horng 1973). Allowing for the 80% crystals the latter are equivalent to a saturation loading of 0.25 to 0.257 g/g Z. This assumes no adsorption on the pellet binder. Jury and Horng are the sole authors who specifically consider adsorption to occur on the binder; many authors may not have considered this point. The isotherms of Cointot et al. (1968) clearly show capillary condensation as saturation is approached. The high values of Breck (1974) may exhibit some of this phenomenon; accordingly a reasonable value of water saturated adsorption within the zeolite pores is postulated to be between 0.25 and 0.265 g/g Z.

Two heats of adsorption are clearly evident in Table 1. Excluding the values of Ulku et al. (2005), [inconsistent with all the other data], the heat of adsorption below a fractional loading $\theta$ of $\sim 0.2$ varies from 100 to 125.5 kJ/mol (Dubinin et al. 1969; Vergnaud et al. 1965; Zhdanov et al. 1981; Breck 1974) and above a $\theta$ of $\sim$0.2, decreases from 74.06 to 50.63 (Breck 1974; Dubinin et al. 1969; Avgul et al. 1968; Jury and Horng 1973; Cointot et al. 1968; Zhdanov et al. 1981). The break point of $\theta \approx 0.2$ is consistent with transition from the $\beta$ cage to the $\alpha$ cage. Dubinin et al. (1969) clearly state that the heat of adsorption is invariant from 0 to 0.2 loading for this system. The differences in the heat of adsorption are reflected in the potential energy of adsorption calculations for the different size cavities illustrating the bifurcation tendencies of this zeolite for adsorption of water.

The isotherm models employed in the literature vary from the simple [Henry] to the complex (Gorbach et al. 2004). Langmuir has been used extensively particularly by workers involved in kinetic column modeling (Cui 2001; Carter and Hussain 1974; Ulku et al. 2005; Gorbach et al. 2004) although it clearly does not fit the data as mentioned by many (Gorbach et al. 2004). Other theories employed are the Polanyi Potentail theory (Cointot et al. 1968; Qin et al. 1980), Dubinin isotherm (Cointot et al. 1968), and 18 models by Gorbach et al. (2004) such as (Henry-Langmuir, Toth, Sips, BET and Aranovich). Jury and Horng (1973) employ a two site Langmuir theory, consisting of a zeolite site and a clay binder site and they attributed approximately 16% of the adsorption to being on the clay binder site.

Dubinin and coworkers did extensive studies on the adsorption of water on NaA (7, 13-22). Differential thermobarometry and gravimetry revealed that a maximum of 4 molecules is strongly bonded in 1 cavity (Mikhailova et al. 1979). The adsorption system NaA-$D_2O$ was observed to produce a doublet structure using ir spectroscopy (Dubinin et al. 1975). The form of the adsorbed water on NaA zeolite surface depended on the degree of water adsorption. At $\leq$2 mmole/g Z ($\theta$ of $\sim$0.2), only one form of water, strongly bound by an ion-dipole interaction, was observed using IR. The frequencies and intensities of the adsorption max. and the adsorption heats change markedly in the region of 2 mmole/g Z (Dubinin et al. 1974). The time for establishing adsorption equilibrium changes depending on the degree of coverage of the zeolite. At 2.3 mmole/g, it passed through a max. corresponding to a block of all the entry windows into the larger cavities by adsorbed water (Kononyuk et al. 1972). NMR studies revealed the presence of strong and weak adsorbent-adsorbate interaction (Deininger et al. 1969). Dilatometry established that adsorption of 6 mmol/cavity caused zeolite expansion of 0.2%, compression of 0.2%, at 16 mmol/cavity, and expansion up to 0.4% at $P/P_s$ of 0.85 (Kononyuk et al. 1971). Kinetic measurements using calorimetry revealed that the time of attainment of equilibrium in this system up to 15% surface filling was tens of times longer than needed to accomplish the equilibrium at filling of the rest of the adsorption space. Two types of adsorption centers were uncovered which differed in the energy of hydration. The strong centers had differential heat of adsorption of 100.4 kJ/mol and the weak ones 62.76 (Dubinin et al. 1969). Glazun et al. (1967) using dielectric measurements of water adsorbed on various ion exchange forms of NaA established that at high concentrations of adsorbed water, the water molecules formed definite structures, the shape of which depend on the nature of the cations involved in the zeolite. Dielectric properties of water at −40 to +20°C reveal that the activation energies and activation entropies increase with increasing water content; they are larger than those for ice at a water content of >5% (Fedorov et al. 1966). Using dielectric measurements, the energies, entropies and free energies of activation of the polarization process of water adsorbed by NaA were calculated and compared with the corresponding thermodynamic functions of ice (Fedorov et al. 1964).

Simontot-Grange et al. (1985) employed microcalorimetry to determine the heat of adsorption and heat capacities of water on 13X, 4A and montmorillonite. Also, they determined adsorption isotherms by a micro-thermogravimetric method. Vergnaud et al. (1965), using NMR, indicate that cavities may contain approximately 8% water (the excess constituting an independent phase external to the zeolite, 1.4% very strongly bonded, 2% in the interior of the small cavities, and 5% inside the large cavities, constituting the least strongly held water. Hino (1977), using HDO molecules in IR studies, observed a band at 3590 cm$^{-1}$ arising from some other type of adsorbed water molecules. Singh and Ruthven (1984) studied adsorption of $D_2O$ and $H_2O$ on 4A zeolite at very low humidity conditions and observed no significant isotopic effect.

### 1.1 Theoretical model

The surprising results obtained by the author influenced him to re-evaluate all the physical properties of the 4A system. The results of this re-evaluation are presented in Table 2 and differ in many aspects from the text by Breck (1974). The dehydrated density was calculated to be 1.897 g/cc using the pseudo unit cell formula weight, Avogadro's number and crystallographic measurements. This is 5% lower than the value of 1.99 g/cc provided by Breck (1974). The maximum number of water molecules is 31 (926/29.91) puc assuming no steric limitations. This is 4 molecules greater than given in the hydrated formula weight (Breck 1974). The saturated loading was calculated using the formula

$$q_{\text{sat crystal}} = \frac{n_{\max} MW_{H_2O}}{\rho N_o V_{\text{unit cell}}} \tag{1}$$

with $n_{\max} = 31$, and provided calculated loadings of 0.261 g/g Z and 0.2088 g/g Linde 4A molecular sieve pellet containing 20% binder (assumed non-adsorbing). This is consistent with the results reported in the literature survey. Using $n_{\max} = 27$ provided an inaccurate saturated loading of 0.227 g/g Z for the zeolite crystals. This supports the conclusion that the cavities retain 31 molecules and that 27 is too low. The specific volume of the respective cages and pseudo unit cell are given in the last line. The total pore volume of 261 cc/kg differs markedly from the 320 cc/kg provided by Breck (1974). Using the density figure of 1.99 g/cc provided by Breck (1974), gives a pore volume of 249 cc/kg.

A general isotherm equation for $n$ sites may be written as

$$\frac{q}{q_{\text{sat}}} = \sum_{i=1}^{n} f_i \theta_i \tag{2}$$

where $q$ is the loading g adsorbate/g pellet, $q_{\text{sat}}$ is the saturated loading g adsorbate/g pellet, $f_i$ is the fraction of sites of type $i$ and $\theta_i$ is the fractional loading on each site. $f_i$ may be considered as the fractional volume of either cage to the total cage volume. Thus $f_\beta$, the ratio of the $\beta$ cage to the total cage volume is $= (150/(150+776)) = 0.162$, and $f_\alpha$ the ratio of the $\alpha$ cage to the total cage volume is $(776/(150+776)) = 0.838$. Further, $q_{\text{sat}}$ may be written as

$$q_{\text{sat}} = \omega q_{\text{sat crystal}} \tag{3}$$

where $\omega$ is the fraction of crystal in the pellet.

The specific equation for water adsorption on 5A zeolite may then be written (assuming no adsorption on the binder) as

$$\frac{q}{q_s} = f_\beta \theta_\beta + f_\alpha \theta_\alpha \tag{4}$$

or

$$\frac{q}{q_s} = 0.162\theta_\beta + 0.838\theta_\alpha \tag{5}$$

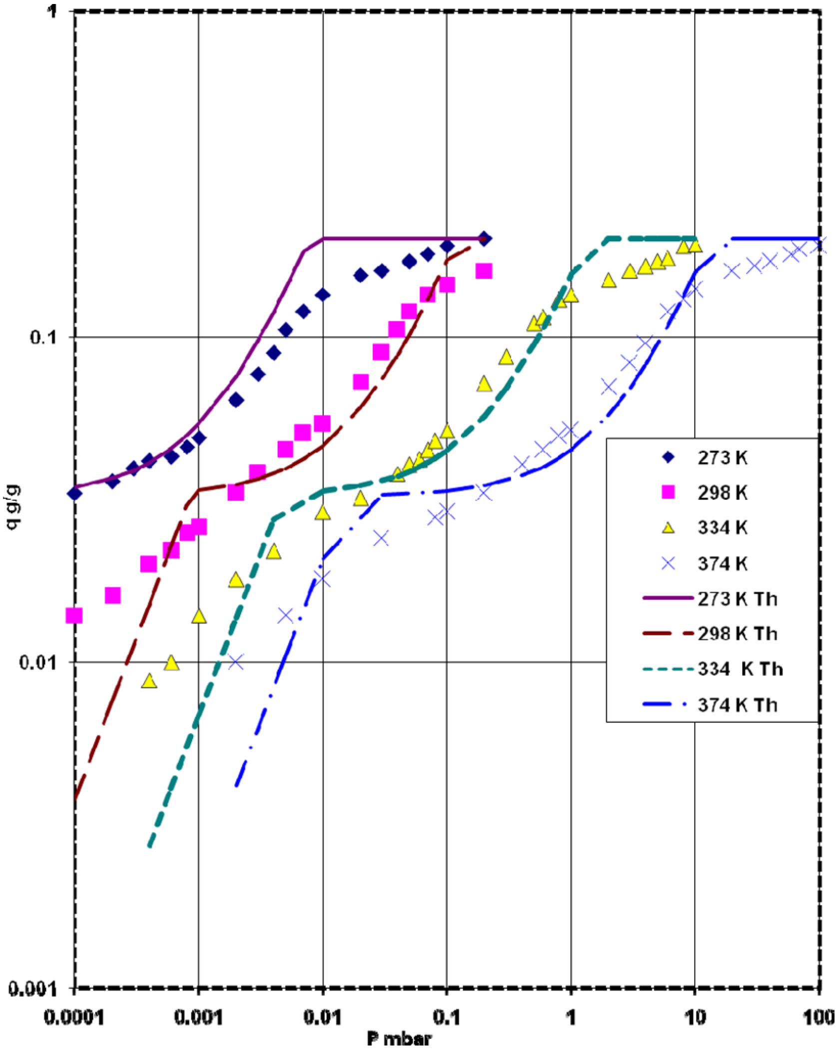
For each site, different isotherm models may be employed. Do (1998) lists well over 50 models in chapters 2 to 4 of his textbook In addition the isotherm model of Ruthven (1984) may be included. This gives $51^2$ or $n^2$ possibilities, equivalent to 2600 isotherm models. In the interests of parsimony, only the simpler models are examined.

### 1.2 Modeling results and application to data

The data of Gorbach et al. (2004) and Morris (1968) shown as data points in Figs. 1a and b respectively, are used to evaluate the best fit model. The author did not have the original data or a digitizer; consequently, the appropriate Figures in the paper by Gorbach et al. (2004) were enlarged many times and the data extracted by hand. The data was fitted using 2-parameter, 3-parameter, and 4-parameter equations. The

**Table 2** Recalculated parameters for water adsorption on 4A zeolite

| | |
|---|---|
| Volume one water molecule @ $\rho = 1$ g/cc | 29.91 Å$^3$ per molecule |
| Maximum water molecules $\beta$ cage | 5 |
| Maximum water molecules $\alpha$ cage | 26 |
| Maximum water molecules puc | 31 |
| 4A Crystals | |
| Dehydrated density | 1.897 g/cc |
| Hydrated density (31 water molecules) | 2.392 g/cc |
| Hydrated density (27 water molecules) | 2.32 g/cc |
| Saturated loading (31 water molecules) | 0.261 g/cc |
| Saturated loading (27 water molecules) | 0.227 g/cc |
| Linde 4A pellets | |
| Saturated Loading (31 water molecules) | 0.2088 g/cc |
| $V_\beta$, $V_\alpha$ , $V_p$ | 42.28, 218.5, 261 cc/kg |



(a)

**Fig. 1** (**a**) Fit of the dual Henry constant model to the data of Gorbach et al. (2004) subject to the restriction that $K_i p \leq 1$. (**b**) Fit of the dual Henry constant model to the data of Morris (1968) subject to the restriction that $K_i p \leq 1$

models were calculated using solver in the EXCEL package. Also the 5 parameter equation of Gorbach et al. (2004) and the model of Jury and Horng (1973) is compared to one of the models derived. In executing the calculation, a relative form of the residual was employed for each isotherm, e.g.,

$$\text{Residual} = \sqrt{\sum_{i=1}^{n}\left(\frac{y_{i,\exp} - y_{i,th}}{y_{i,\exp}}\right)^2} \qquad (6)$$

This places emphasis on the whole spectrum of the isotherm, whereas an absolute criterion is limited to the higher concentrations.

## 2 2-Parameter models

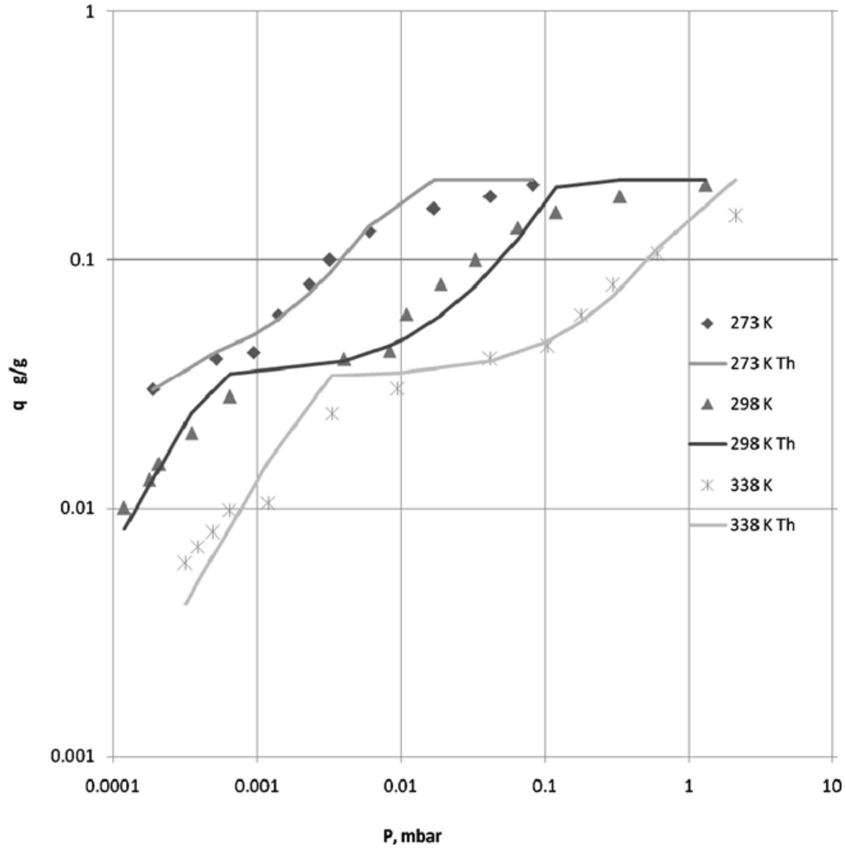
Three 2-parameter models are evaluated, a dual site Henry constant model, a dual site Langmuir (LL) model and a combined Ruthven-Langmuir (RL) model. Dual implies a similar isotherm model is applied to both sites. The dual Henry constant equation is

$$\frac{q}{q_s} = 0.162 K_\beta p + 0.838 K_\alpha p \qquad (7)$$

subject to the restriction that $K_i p \leq 1$, $i = \alpha$ or $\beta$. For this data, $q_s$ is 0.2088 g/g pellet. The saturation loading for the $\beta$ cage is then 0.0324 and for the $\alpha$ cage is 0.1676 g/g pellet. For the data at 273 K, the $\beta$ cage appears fully saturated as no data exists below a loading of 0.0324 g/g. Hence, this isotherm temperature data may only be modeled for the $\alpha$ cage. This latter statement implies that the $\beta$ cage practically saturates before any significant adsorption occurs in the $\alpha$ cage. The Henry constants for both cages are defined by

$$H_i = f_i K_i q_s \qquad (8)$$

**Fig. 1** (Continued)



(b)

with $i = 1, 2$ representing the $\beta$ and $\alpha$ cages respectively. In principle the Henry constant for the $\alpha$ cage should be represented by

$$H_\alpha = H_\beta + H_\alpha \tag{9}$$

However, inspection of the van't Hoff plot in Fig. 6 reveals that $H_\alpha$ is approximately two orders of magnitude less than $H_\beta$ so that utilizing (8) instead of (9) introduces negligible error if an assumption of a frozen solid is applied to the $\beta$ cage.

Two points may clearly be established from Figs. 1a and b. The experimental data contains a point of inflection at a loading of approximately 0.03 g/g. This is consistent with the hypothesis regarding the large difference in the Henry constants and that the $\beta$ cage saturates first before significant adsorption occurs in the $\alpha$ cage. Secondly, the slope of the equilibrium data at low loading for the $\beta$ cage is not equal to 1 for the Gorbach et al. data (2004) as is expected for sorbates obeying Henry's Law. The data of Morris (1968) more closely approaches a Henry Law limit in the $\beta$ cage. This can clearly be observed by comparing the difference that arises between the predicted Henry plots of slope 1 and experimental plots which have an approximate slope of about 0.6 for the Gorbach et al. data (2004) and 1 for the Morris (1968) data. This suggests that a homogeneous isotherm will not fit this section of the data in the case of Gorbach et al's data (2005); rather a heterogeneous model may have to be employed. However, a homogeneous model may be used to fit the Morris data. The fit of the dual Henry constants model subject to the restriction mentioned is not good for the Gorbach et al. (2004) data but is surprisingly good for the Morris (1968) data.

The fit of the dual Langmuir model is shown in Figs. 2a and b and the optimized parameters are presented in Table 3.

$$\frac{q}{q_s} = 0.162\frac{K_\beta p}{1 + K_\beta p} + 0.838\frac{K_\alpha p}{1 + K_\alpha p} \tag{10}$$

The fit is excellent in the range $0.15 < \theta < 1$ but is poor below $\theta = 0.15$ for the Gorbach et al. (2004) data. This is expected as the Langmuir model reduces to Henry's law in the limit but the data does not. As a consequence, the residual is much larger for this model than for the next 3 models involving the Gorbach et al. (2004) data. However, the fit of the Morris data is good. This substantiates the difference of approach established above. Further, the fit of the dual Langmuir site model to the Morris data is so good, that the need for an alternate model is not justified and is not attempted

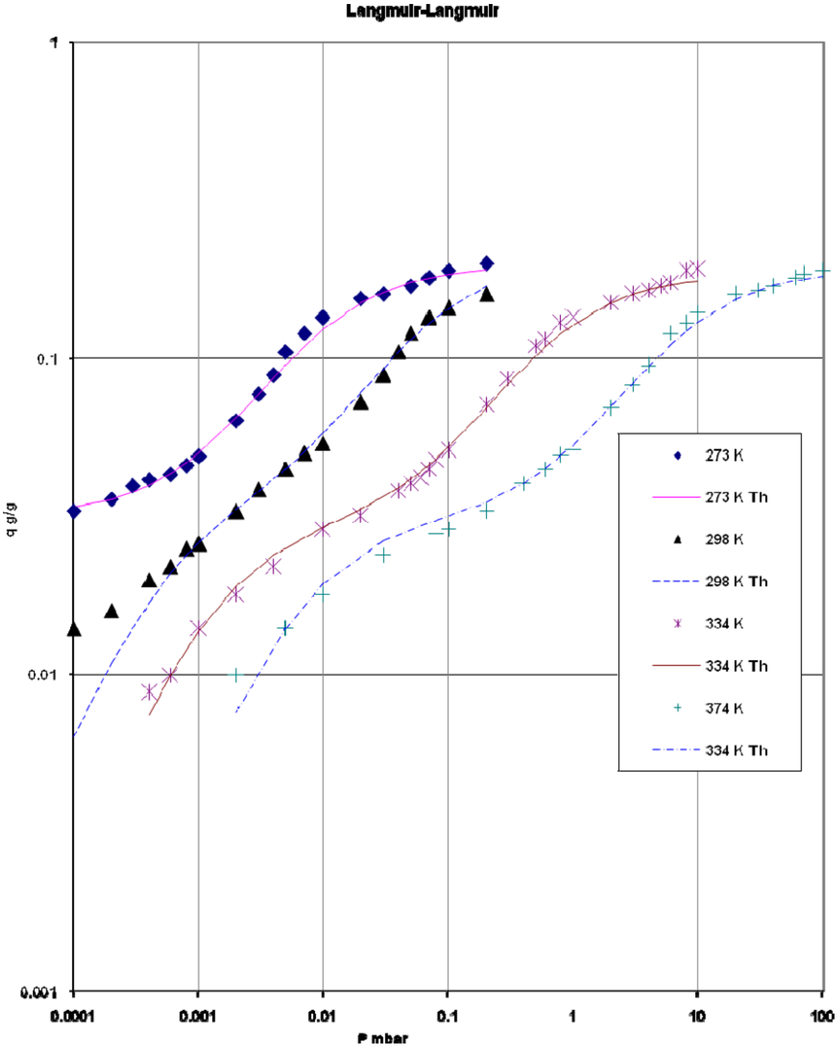


**Fig. 2** (**a**) Fit of the Langmuir-Langmuir model to the data of Gorbach et al. (2004). (**b**) Fit of the Langmuir-Langmuir model to the data of Morris (1968)

for this set of data. The dual Langmuir site model is so simple and accurate for $\theta$ exceeding 15% that it is probably the recommended model to use in diffusion studies modeling.

The Henry constant equations are expressed in the usual van't Hoff form using

$$H_i = H_{oi}\exp(-\Delta H_i/RT) \tag{11}$$

The final 2 parameter model examined is the Ruthven model in the $\beta$ cage and the Langmuir model in the $\alpha$ cage. The isotherm equation is

$$\frac{q}{q_s} = 0.0324 \times \frac{K_\beta p + (K_\beta p)^2(1-2\beta_H/v)^2 + \cdots + (K_\beta p)^m(1-m\beta_H/v)^m/(m-1)!}{1+K_\beta p + \frac{1}{2}(K_\beta p)^2(1-2\beta_H/v)^2 + \cdots + (K_\beta p)^m(1-m\beta_H/v)^m/m!} + 0.838\frac{K_\alpha p}{1+K_\alpha p} \tag{12}$$

where $\beta_H$ is the volume of the water molecule [29.91 Å$^3$], and $v$ is the volume of the $\beta$ cage [150 Å$^3$]. The factor $f_\beta$ is reduced by $m_{\max}$ the maximum number of molecules of water admitted to the $\beta$ cage. The maximum value of $m$ is the integer value of $v/\beta_H$ which is 5. The fit of the model is shown in Fig. 3 and the optimized parameters for the $K_i$ in Table 3. The residual for this case is much better than the dual Langmuir case for the Gorbach et al. (2004) data and the fit is excellent even in the Henry's law region. It is clear that the interaction between adsorbed molecules results in the apparent heterogeneous behavior, and that the dominant interaction is due to the reduction in free volume in the sodalite cage.

## 3 3-Parameter model

The 3 parameter model examined was the use of the Toth model in the $\beta$ cage and the Langmuir (TL) model in the $\alpha$ cage. The isotherm equation is

$$\frac{q}{q_s} = 0.162\frac{p}{(m_\beta + p^{t_\beta})^{1/t_\beta}} + 0.838\frac{K_\alpha p}{1+K_\alpha p} \tag{13}$$

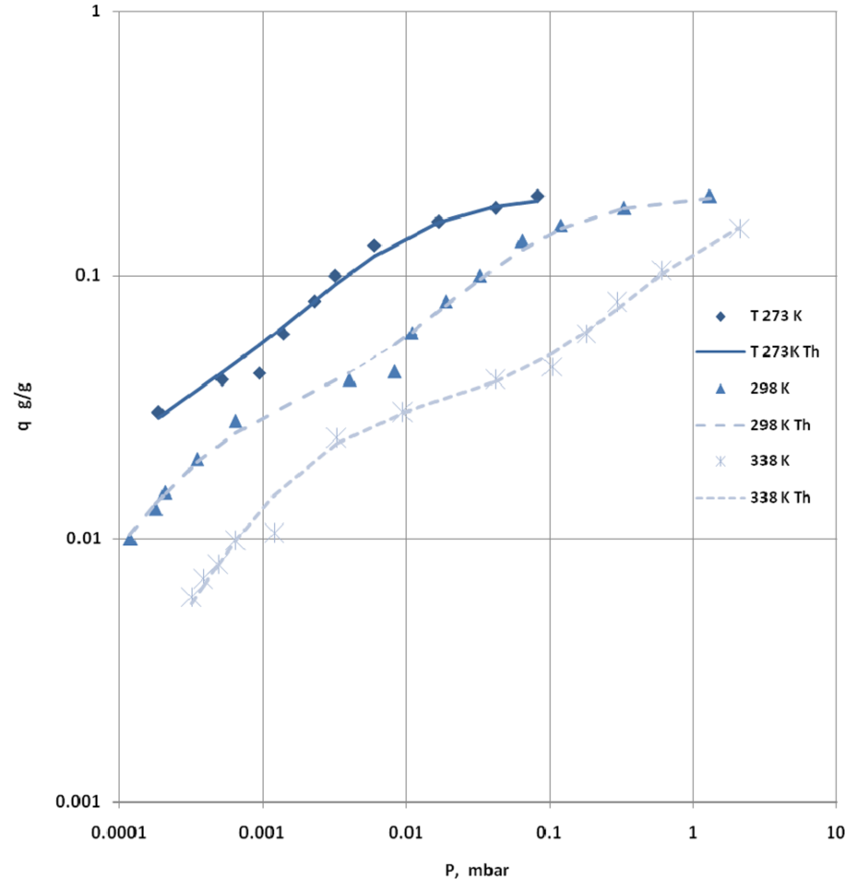


**Fig. 2** (Continued)

The 3 parameters optimized were, $m_\beta$ the equilibrium parameter, $t_\beta$ the heterogeneity parameter in the $\beta$ cage, and the equilibrium parameter $K_\alpha$ in the $\alpha$ cage. The fit of the model is shown in Fig. 4 and the optimized parameters are given in Table 3. Of the cases considered so far, this has the lowest residual as befits a 3 parameter model.

Other 2 parameter heterogeneous models could also have been used for the $\beta$ cage such as the Freundlich, Sips or Unilan isotherms. These were not examined in the interests of brevity. Further, the Toth isotherm was one of the major isotherms used by Valenzuela and Myers (1989) in their adsorption equilibrium handbook, and hence it was not deemed necessary to review more heterogeneous cases. A secondary reason for not using other models is the considerations that will arise from analysis of the van't Hoff data.

## 4 4-Parameter models

The 4 parameter model examined was the application of the Toth isotherm model (TT) to both cages. The isotherm equation is

$$\frac{q}{q_s} = 0.162\frac{p}{(m_\beta + p^{t_\beta})^{1/t_\beta}} + 0.838\frac{p}{(m_\alpha + p^{t_\alpha})^{1/t_\alpha}} \tag{14}$$

The 4 parameters optimized were, $m_\beta$ the equilibrium parameter, $t_\beta$ the heterogeneity parameter in the $\beta$ cage, $m_\alpha$ the equilibrium parameter and $t_\alpha$ the heterogeneity parameter in the $\alpha$ cage. The fit of the model is shown in Fig. 5 and the optimized parameters are given in Table 3. This is the best model of all the models considered for the Gorbach et al. (2004) data. An interesting observation is that $t_\alpha$ is approximately 1 indicating that the Toth isotherm is similar to a Langmuir in the $\alpha$ cage. Indeed the residuals are the same for Toth-Toth model as for the Toth-Langmuir model for these isotherms. This suggests that the added complication introduced by an extra parameter is not justified. Therefore the 3 parameter Toth-Langmuir model is probably the optimum model for the Gorbach et al. data.

### 4.1 Literature models similar to the above

Two models that of Gorbach et al. (2004) and Jury and Horng (1973) have many similarities with the dual site Langmuir model. The optimized Gorbach et al. (2004) model is

$$\frac{q}{q_s} = b_0(T)\frac{b_1(T)p + b_2(T)p^2}{1 + b_3(T)p + b_4(T)p^2} \tag{15}$$

**Table 3** Regressed parameters for two models

$\beta$ cage Langmuir-$\alpha$ cage Langmuir: Data Gorbach et al. (2004)

| $T$ K | $q_s$ | $K_\beta$ | $K_\alpha$ | $H_\beta$ | $H_\alpha$ | Residual |
|---|---|---|---|---|---|---|
| 273 | 0.1974 | – | 124.86 | – | 20.660 | 0.0269 |
| 298 | 0.2300 | 2039.6 | 12.422 | 76.003 | 2.395 | 0.1151 |
| 334 | 0.1844 | 818.4 | 1.7667 | 24.444 | 0.2730 | 0.0740 |
| 374 | 0.1925 | 160.22 | 0.1616 | 4.996 | 0.0260 | 0.0987 |

$q_s = 0.2011$ g/g $H_{0\beta} = 1.3667\text{E-}04$ $-\Delta H_\beta = 33.01$ $H_{0\alpha} = 5.2946\text{E-}10$ $-\Delta H_\alpha = 55.31$

$\beta$ cage Ruthven-$\alpha$ cage Langmuir: Data Gorbach et al. (2004)

| $T$ K | $q_s$ | $K_\beta$ | $K_\alpha$ | $H_\beta$ | $H_\alpha$ | Residual |
|---|---|---|---|---|---|---|
| 273 | 0.2120 | – | 138.66 | – | 24.63 | 0.995 |
| 298 | 0.2179 | 88306 | 18.25 | 3117 | 3.33 | 0.772 |
| 334 | 0.2057 | 8799 | 1.8155 | 293.2 | 0.313 | 1.124 |
| 374 | 0.2061 | 2336 | 0.1728 | 78.03 | 0.029 | 0.8725 |

$q_s = 0.2104$ g/g $H_{0\beta} = 1.6053\text{E-}04$ $-\Delta H_\beta = 41.12$ $H_{0\alpha} = 4.042\text{E-}10$ $-\Delta H_\alpha = 55.16$

$\beta$ cage Toth-$\alpha$ cage Langmuir: Data Gorbach et al. (2004)

| $T$ K | $q_s$ | $b_\beta$ | $t_\beta$ | $H_\beta$ | $K_\alpha$ | $H_\alpha$ | Residual |
|---|---|---|---|---|---|---|---|
| 273 | 0.1997 | – | – | – | 130.222 | 21.797 | 0.616 |
| 298 | 0.1883 | 0.002064 | 0.65 | 412.32 | 22.1407 | 3.4938 | 0.8007 |
| 334 | 0.1915 | 0.00765 | 0.664 | 47.64 | 1.7252 | 0.2768 | 0.7674 |
| 374 | 0.1931 | 0.02106 | 0.65 | 11.872 | 0.1706 | 0.0275 | 0.6248 |

$q_s = 0.1932$ g/g $H_{0\beta} = 9.3713\text{E-}06$ $-\Delta H_\beta = 43.39$ $H_{0\alpha} = 3.9862\text{E-}10$ $-\Delta H_\alpha = 56.38$

$\beta$ cage Toth-$\alpha$ cage Toth: Data Gorbach et al. (2004)

| $T$ K | $q_s$ | $b_\beta$ | $t_\beta$ | $H_\beta$ | $b_\alpha$ | $t_\alpha$ | $H_\alpha$ | Residual |
|---|---|---|---|---|---|---|---|---|
| 273 | 0.1997 | – | – | – | 7.68E-03 | 1 | 21.80 | 0.6160 |
| 298 | 0.2059 | 7.740E-03 | 0.463 | 1200 | 5.64E-02 | 0.969 | 3.35 | 0.6911 |
| 334 | 0.1915 | 7.658E-03 | 0.664 | 47.64 | 5.796E-01 | 1 | 0.2769 | 0.7674 |
| 374 | 0.1978 | 3.134E-02 | 0.539 | 19.64 | 6.121E-0 | 1 | 0.0271 | 0.4658 |

$q_s = 0.1987$ g/g $H_{0\beta} = 1.1414\text{E-}06$ $-\Delta H_\beta = 50.66$ $H_{0\alpha} = 3.926\text{E-}10$ $-\Delta H_\alpha = 56.38$

$\beta$ cage Langmuir-$\alpha$ cage Langmuir: Morris (1968)

| $T$ K | $q_s$ | $K_\beta$ | $K_\alpha$ | $H_\beta$ | $H_\alpha$ | Residual |
|---|---|---|---|---|---|---|
| 273 | 0.2088 | – | 157.7799 | – | 27.6078 | 0.0727 |
| 298 | 0.2088 | 3464.6968 | 17.1486 | 117.186 | 3.0006 | 0.0718 |
| 3384 | 0.2088 | 617.4956 | 1.0326 | 20.8855 | 0.1807 | 0.1047 |

$q_s = 0.2088$ g/g $H_{0\beta} = 5.4899\text{E-}05$ $-\Delta H_\beta = 36.11$ $H_{0\alpha} = 71.2144\text{E-}10$ $-\Delta H_\alpha = 59.33$

which may be rearranged as

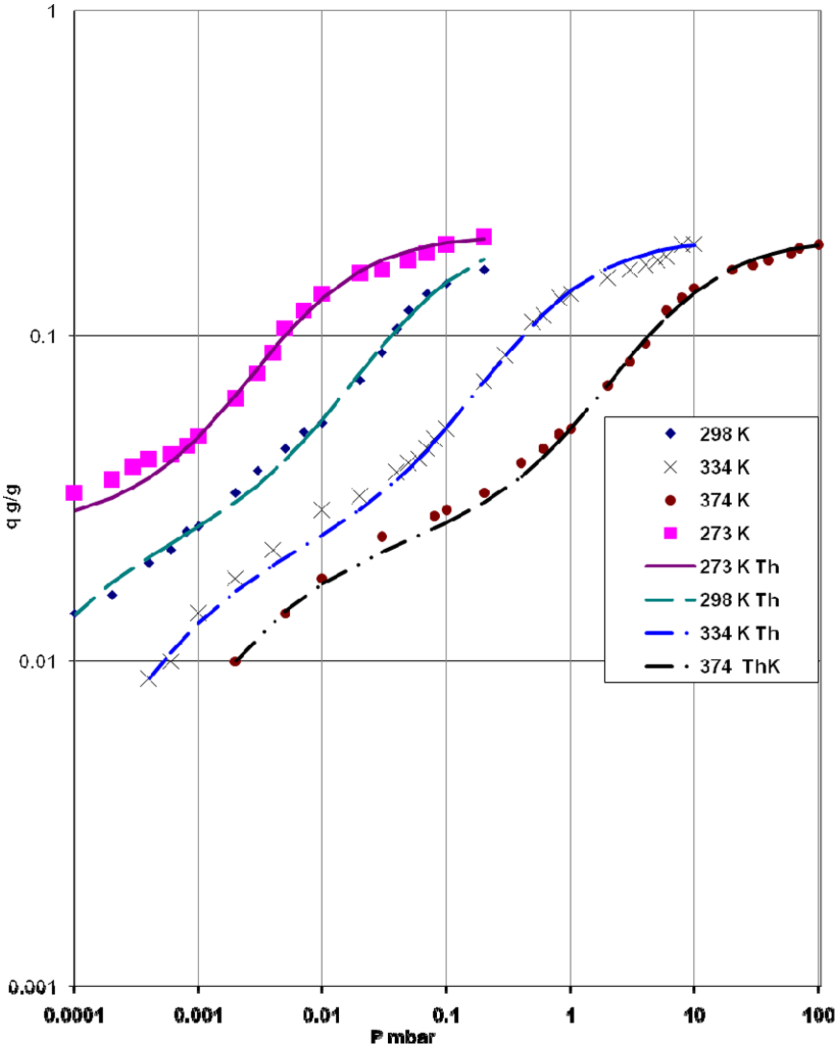
$$\frac{q}{q_s b_0(T)} = \frac{b_1(T)p + b_2(T)p^2}{1 + b_3(T)p + b_4(T)p^2} \tag{16}$$

The dual site Langmuir model may be rearranged to give

$$\frac{q}{q_s} = \frac{(f_\beta K_\beta + f_\alpha K_\beta)p + K_\beta K_\alpha p^2}{1 + (K_\beta + K_\alpha)p + K_\beta K_\alpha p^2} \tag{17}$$

The $b_0(T)$ is similar to a density variation of the adsorbed phase. This may be significant as there are 12 different ice phases existing under very high pressures having densities up to 1.25 g/cc for water. In the dual site Langmuir model it is set equal to 1. It is not possible to compare $b_1(T)$ and $b_3(T)$ to the dual Langmuir model as sum of exponentials are not additive. However it is observed that $b_2(T)$ and $b_4(T)$ are similar to the product $K_\beta K_\alpha$. The pre-exponential factors are very similar as are the sum of the dimensionless

**Fig. 3** Fit of the Ruthven-Langmuir model to data of Gorbach et al. (2004)



heats of adsorption in Table 4 evaluated at 273.25 K, the $T_0$ value used by Gorbach et al. (2004). The logical conclusion is that both models are very similar in some terms and that the optimized constants are approximately the same. This is an important conclusion when the entropy of adsorption is considered.

Jury and Horng (1973) studied the adsorption of water on 4A Linde pellets in a packed bed. Unfortunately they reported their equilibrium results as $q$ versus absolute humidity on a regular plot which is useless for modeling as the low pressure data is indeterminate. They found the Langmuir system did not work. Subsequently they used a two site Langmuir, one for the clay binder and one for the zeolite. The equation used was

$$W = \frac{A_L B_L X_h}{1 + B_L X_h} + \frac{A_h B_h X_h}{1 + B_h X_h} \tag{18}$$

where the first term is for the clay binder and the second is for the zeolite and $W$ is mass adsorbed, in g/g pellet. For $X_h$ they used the Hey approximation

$$X_h = \frac{e^{A/T}}{\sqrt{T}} p \tag{19}$$

and they assumed

$$X_h = X_L \tag{20}$$

They found the optimized parameters to be: $A_h = 0.1579$, $B_h = 6.371\text{E-}9$, $A_L = 0.0479$, $B_L = 3.095\text{E-}11$ and $A = 7509$. Their equations reduce to the simplified model presented in Table 5.

For comparison with this work, the values $H_{0,\text{clay}}$ and $H_{0,\text{zeolite}}$ are given in Table 5 evaluated at 298 K. For the Langmuir-Langmuir model for this study, the value of $H_{0,\alpha}$ is $5.29468 \times 10^{-10}$ and $H_{0,\beta}$ is $1.3667 \times 10^{-04}$. It is observed that their results are in close proximity with this work

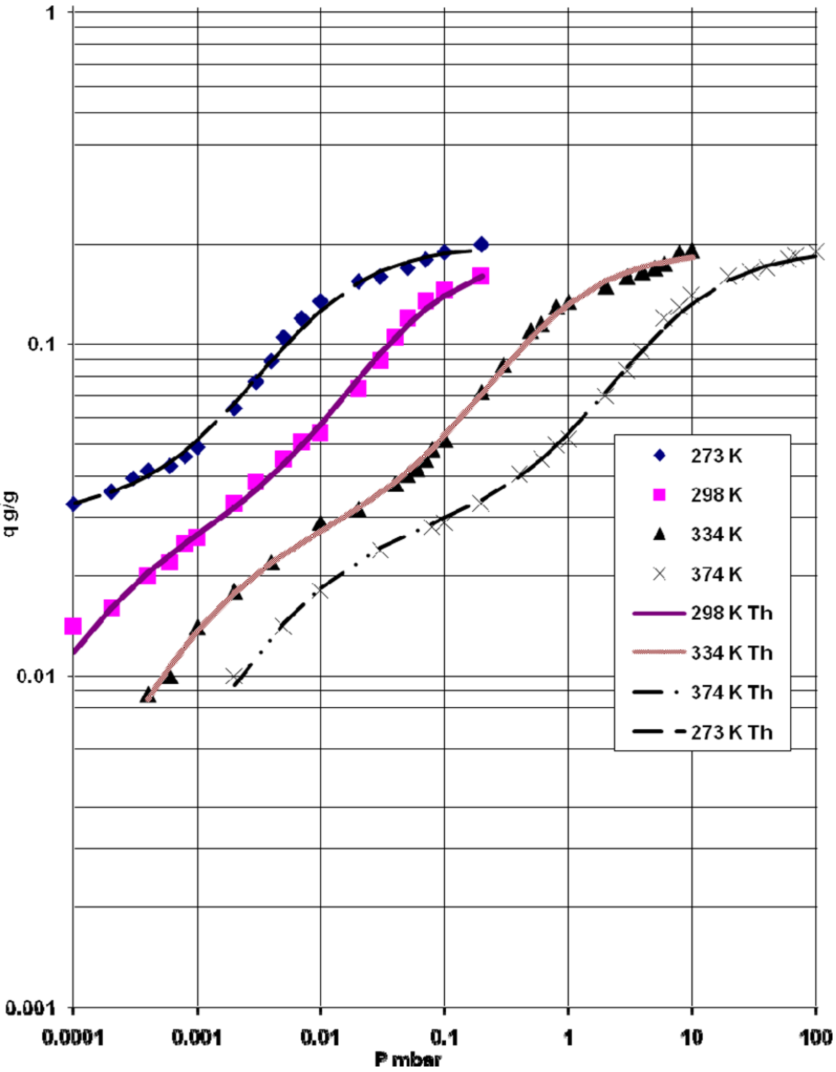


**Fig. 4** Fit of the Toth-Langmuir model to data of Gorbach et al. (2004)

for the $\alpha$ cage. The $\beta$ cage cannot be evaluated as their results are for a clay binder and differ by over 10 orders of magnitude from the results in this study. The author ran a simulation with Jury and Horng's parameters from 2 mm Hg to 750 mm Hg. The loading on the crystallites is constant at 0.157 g/g. However, the sorption on the clay starts low at 0.0084 rising to 0.047 g/g implying at low pressure little is adsorbed on the clay. This is the reverse of what is observed in this study. In this study the small beta cage saturated first and then the alpha cage started to fill up. The surprising result is that the sum of their loadings at high pressure, 0.205 g/g. is approaching the saturation limit for the zeolite alone. This implies that their modelis filling the two cavities rather than the alpha cage and a clay binder as the clay binder can have any arbitrary loading. It also tends to show that their adsorbent was properly regenerated for both cages. The authors also indicate that the sorption efficiency (initial slopes) is about 2,700 times greater for the zeolite crystals than for the clay binder, implying that the loading on the crystallites saturates first. The puzzle is why there is 8 to 10 orders of magnitude of difference if allowance is made for a slight difference in the exponential factor. The reason for this difference is not clear. It may be an artifact of the optimization procedure or a local minima of the optimization procedure.

## 4.2 Van't Hoff Plot

The Henry constants for the four models, dual Langmuir, dual Toth, Ruthven-Langmuir and Toth Langmuir are plotted in Fig. 6 semi-logarithmically as $H$ versus $1/T$ from the data in Table 3. Also plotted is the LL fit for the Morris (1968) and the fit for the Jury and Horng (1973) model. It is clear that the Henry constants for the $\alpha$ cage are practically indistinguishable from each other and are basically model independent. The calculated $H_\alpha$ for the data of Jury and Horng (1973) are plotted in Fig. 6. And exhibit a slightly stronger temperature dependence possibly due to the $\sqrt{T}$ term. It also implies that the data in this region is pretty well defined. So we can conclude that the

**Fig. 5** Fit of the Toth-Toth model to data of Gorbach et al. (2004)

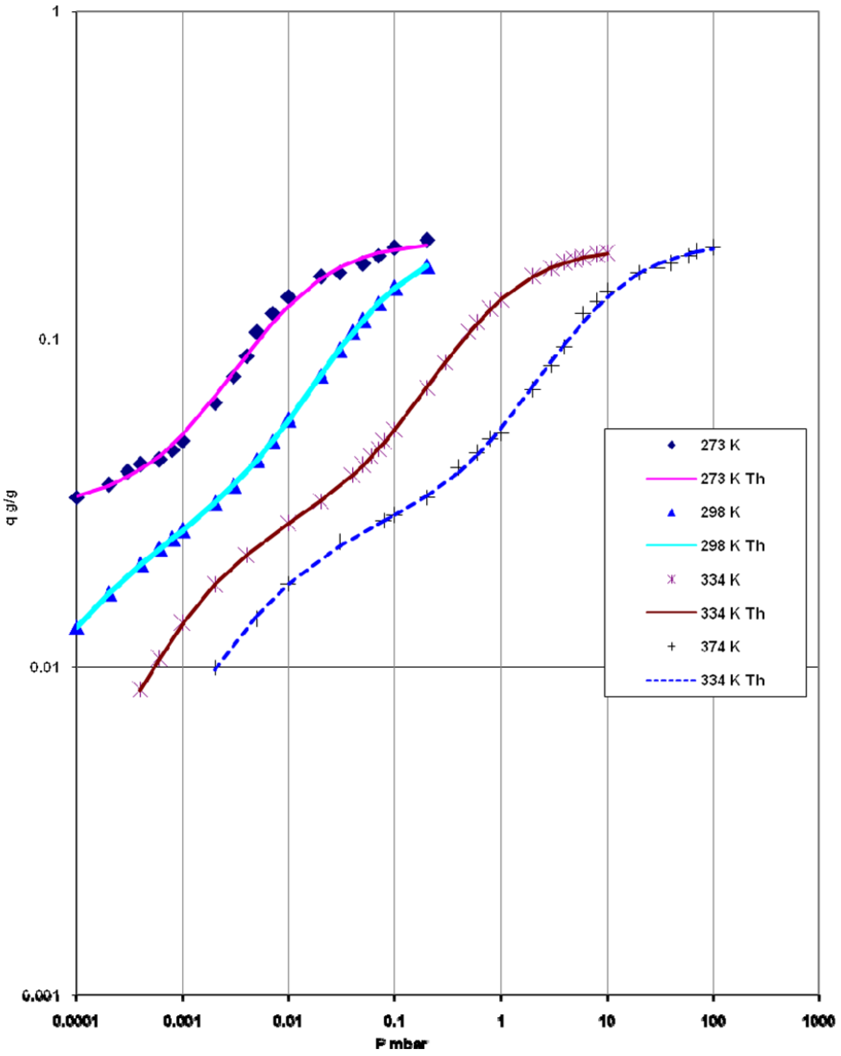


**Table 4** Comparison of Gorbach et al. model to dual site Langmuir model

| Gorbach et al. model | Dual site Langmuir model |
|---|---|
| $b_0$(T) | 1 |
| $b_1$(T) | $f_\beta K_\beta + f_\alpha K_\alpha$ |
| $b_2$(T) | $K_\beta K_\alpha$ |
| $b_3$(T) | $K_\beta + K_\alpha$ |
| $b_4$(T) | $K_\beta K_\alpha$ |
| $b_{2,0} = 1.7532 \times 10^{-10}$ mbar$^{-1}$ | $K_{\beta 0} K_{\alpha 0} = 4.096 \times 10^{-11}$ |
| $b_{4,0} = 1.2243 \times 10^{-11}$ mbar$^{-1}$ | $T_0 = 273.25$ K |
| $b_{2,T} = 41.3509$ | $-\frac{\Delta H_\beta}{RT_0} - \frac{\Delta H_\alpha}{RT_0} = 37.87$ |
| $b_{4,T} = 41.1549$ | |

**Table 5** Model of Jury and Horng

$q_s = A_L + A_h = 0.2058$ g/g

$f_{\text{clay}} = 0.232$

$f_{\text{zeolite}} = 0.768$

$H_{\text{clay}} = A_L B_L \frac{e^{A/T}}{\sqrt{T}}$

$H_{\text{zeolite}} = A_h B_h \frac{e^{A/T}}{\sqrt{T}}$

$H_{0,\text{clay}} = \frac{A_L B_L}{\sqrt{T}} = 8.59 \times 10^{-14}$

$H_{0,\text{zeolite}} = \frac{A_h B_h}{\sqrt{T}} = 3.3377 \times 10^{-11}$

$-\Delta H = RA = 62.43$ kJ/mol

$H_{0,\alpha} = 5.294 \times 10^{-10}$

$H_{0,\beta} = 1.3667 \times 10^{-4}$

$-\Delta H_{0,\alpha} = 55.31, 59.33$ kJ/mol

Henry constants for the $\alpha$ cage are reasonably well defined.

However the plots for the $\beta$ cage show a fairly random variation in the Henry constant. The Henry constants vary by one to two orders of magnitude. The smallest values are given by the Langmuir-Langmuir plot which was observed inapplicable in the Henry's Law region for the Gorbach et al. (2004) data but applicable for the Morris (1968) data. The largest values are for the Ruthven-Langmuir model and the smallest values are for the Langmuir-Langmuir,

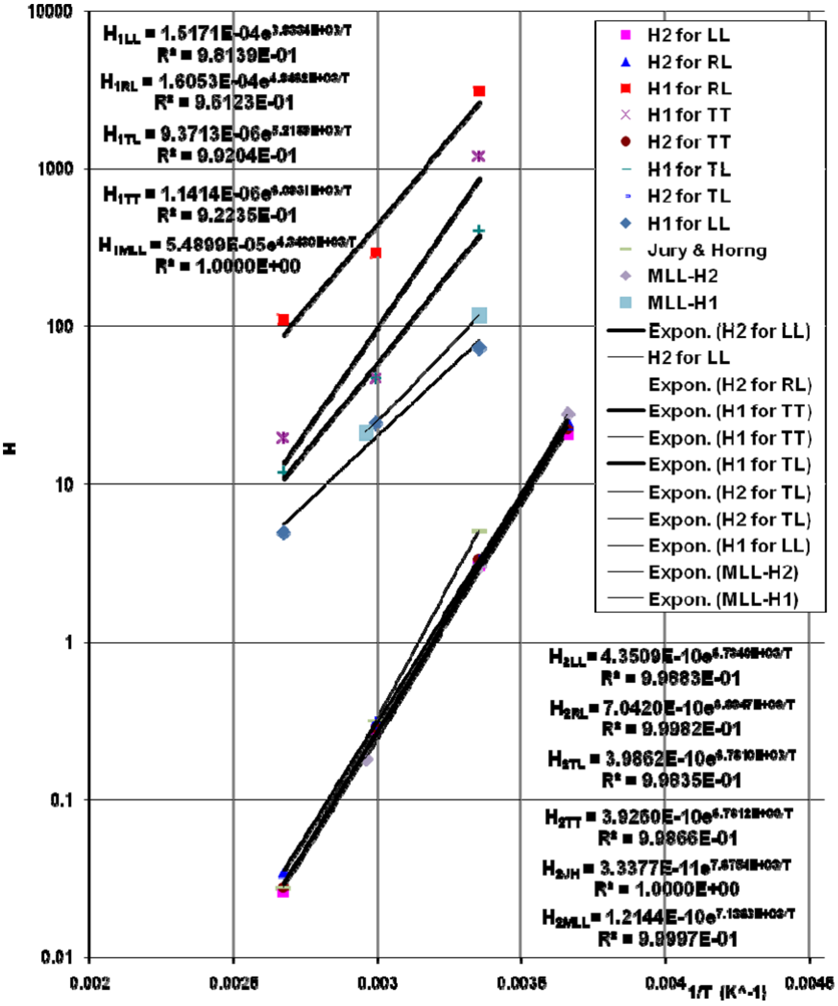


**Fig. 6** van't Hoff plot of Henry Constants

with the Toth-Toth values intermediate between these two cases.

Further the heats of adsorption for the two cages are the reverse of that expected. For the $\alpha$ cage the heats of adsorption are approximately 55 kJ/mol whereas for the $\beta$ cage the model values are 33 to 50 kcal/mole. Breck gives the value of more than 125 kJ/mol for the $\beta$ cage and 73 kJ/mol for the $\alpha$ cages respectively. Dubinin et al. (1969) provides heats of adsorption of 102.5 kJ/mol and 62.75 kJ/mol for the $\beta$ cage. Compared to the calorimetric results, the values of heats of adsorption obtained for the $\beta$ cage in this study appear far too low but appear consistent with that obtained by Gorbach et al. (2004).

### 4.3 Entropic considerations

To calculate the differential entropy of sorption at zero loading, it is necessary to use the dimensionless equilibrium constant defined for each cavity as

$$c_s = K_{c\alpha} c_g \tag{21}$$

and

$$c_s = K_{c\beta} c_g \tag{22}$$

where $c_s$ and $c_g$ are in units of moles/cc pore, and $K_{c\alpha}$ and $K_{c\beta}$ are the dimensionless equilibrium constants. $K_{c\alpha}$ and $K_{c\beta}$ may then be expressed as

$$K_{ci} = e^{\Delta S_i/R} e^{-\Delta H_i/RT} \quad i = \alpha \text{ or } \beta \tag{23}$$

so that

$$\frac{\Delta S_i}{R} = \ln K_{ci} + \frac{\Delta H_i}{RT} = \ln K_{ci0} \quad i = \alpha \text{ or } \beta \tag{24}$$

This definition is formally equivalent to that used by Myers (2004) and is consistent with Barrer's procedure (1978). $K_{ci0}$ is then equated to the pre-exponential factor of the Henry constant $H$ or the equilibrium parameter $K$ to give

$$K_{ci0} = \frac{RT \rho_z V_z}{\omega M W_{H_2O} V_i} H_i \quad i = \alpha \text{ or } \beta \tag{25}$$

$$K_{ci0} = \frac{q_s RT \rho_z V_z}{\omega MW_{H_2O} V_p} K_{i0} \quad i = \alpha \text{ or } \beta \tag{26}$$

where $q_s$ is the saturation loading in g water/g pellet, $R$ is the gas constant $= 82.10\text{E}+03$ mbar.cc/moles.K, $T$ is temperature in Kelvin, $\rho_z$ is the density of the dehydrated zeolite [$= 1.897$ g/cc], $\omega$ is the mass fraction of crystal in the pellet, $MW$ is the molecular weight of water and $V_p/V_z$ is the ratio of the unit cell pore volume to the unit cell zeolite volume, and $K_{i0}$ is the pre-exponential factor for the equilibrium parameter $K_i$. The ratio of the pore volume to the zeolite volume can be expresses as the void fraction [$= 0.47$ Breck or 0.49 (calculated)], or more precisely as the ratio of each cage volume to the pseudo unit cell volume. For the $\beta$ cages this is

$$\frac{V_\beta}{V_z} = \frac{151}{1870} = 0.08075 \tag{27}$$

and for the $\alpha$ cage

$$\frac{V_\alpha}{V_z} = \frac{776}{1870} = 0.415 \tag{28}$$

This gives, using the $\beta$ cage volume

$$K_{c\beta_0} = 21740.T K_{\beta 0} \tag{29}$$

and the $\alpha$ cage volume

$$K_{c\alpha_0} = 4230.T K_{\alpha 0} \tag{30}$$

The calculated standard enthalpies and entropies of sorption are given in Table 6 together with results extracted from the paper of Myers (2004) for various molecules and zeolites. The values are calculated for the Henry law region for one molecule only in each cavity. This is appropriate for the $\beta$ cage as the Henry constants are greater by a factor of 100 than those in the $\alpha$ cage thus making the $\alpha$ cage phenomena inconsequential. However to implement the calculation for the $\alpha$ cage, it is assumed that the $\beta$ cage is frozen in a saturated condition, and that the $\alpha$ cage is isolated, unaffected by the phenomena occurring in the $\beta$ cage. This is an assumption that may not be justified.

The enthalpy of sorption calculated from the regressed equations varies from 33.01 to 50.66 kj/mol for the $\beta$ cage whereas for the $\alpha$ cage, the enthalpy of sorption varies from 55.16 to 56.36 kj/mol for the four model isotherms employed. The standard deviation is very high for the $\beta$ cage at 2.36 kJ/mol whereas it is very low for the $\alpha$ cage at 0.28 kJ/mol indicating that the models differ significantly in the $\beta$ cage whereas they all reduce to the Langmuir form for the $\alpha$ cage. As noted earlier, the data of Morris appears to be different from that of Gorbach et al. (2004) in this region. Recall that the sum of the enthalpies was in agreement with two constants in the model of Gorbach et al. (2004)

A surprising result is that the standard enthalpy of sorption is lower for the smaller $\beta$ cage. The dimensionless standard entropies of sorption are positive for the $\beta$ cage between 3.81 and 8.76, a physical impossibility, and negative between $-5.21$ and $-5.78$ for the $\alpha$ cage, as expected. The physical impossibility of a positive differential entropy change implies that an assumption hitherto acceptable has become invalid. The dimensionless equilibrium constant is given by:

$$K_c = e^{-\Delta G/RT} = e^{\Delta S/R} e^{-\Delta H/RT} \tag{31}$$

In this equation the traditional assumption has been that the major temperature effect is due to the inverse temperature relationship in the enthalpy term and that the standard entropy and enthalpy at zero loading are major temperature invariant. But this assumption has produced a physical impossibility for entropy differential in the $\beta$ cage, and must now be revised based on factual data.

The calorimetric measurements of the enthalpy of sorption in the $\beta$ cage by Dubinin and co-workers (1969) and by Vergnaud et al. (1965) indicate that the enthalpy of sorption is 100 or 105 kJ/mol. Dubinin and coworkers also found it was invariant up to saturation in the $\beta$ cage. Taking the average value of 102.5 kJ/mol implies that the standard differential entropy of sorption varies significantly with temperature. This arises because the normal $\ln K$ versus $1/T$ plots for the $\beta$ cage produced slopes for standard enthalpy of sorption about 1/3rd that measured calorimetrically. The standard enthalpy of sorption for the $\alpha$ cage measured calorimetrically is 14 to 15 kJ/mol similar to the values calculated from both the isosteric means of measurement and isotherm modeling as given in Table 3. Further the calorimetric results are what is expected based on the size of the two cavities.

The standard dimensionless differential entropy of sorption is recalculated based on a standard enthalpy of sorption of 102.5 kJ/mol and the results at 298 K are presented in Table 6 in lines 11 to 17. The entropy of sorption is now negative, varying between 16.02 to 20.97, as is expected. For the Langmuir-Langmuir model the enthalpy was also calculated from the data at 334 and 378 K and found to be 13.4 kJ/mol and 10.70 kJ/mol respectively. Thus we see a substantial reduction in the differential dimensionless standard entropy from 16.18 to 10.70 as the temperature rises from 298 to 374 K.

Is there any supporting evidence for these results. The results are compared to the study of Myers (2004) to the ZSM-22 (TON) zeolite. This zeolite has a pore volume of 69 cc/kg analogous to the 46.17 cc/kg of the $\beta$ cage.

Comparing the results to the sorption of $n$-$C_8H_{18}$, the standard enthalpy of sorption, the dimensionless standard enthalpy of sorption and the dimensionless entropy of sorption are similar. The major difference is that $n$-octane is

**Table 6** Comparison of dimensionless heats and entropies of adsorption

| (a) $H_2O$ on 4A | | $\beta$ cage | | | $\alpha$ cage | | |
|---|---|---|---|---|---|---|---|
| Calculated | | $V_\beta = 46.17$ cc/kg | | | $V_\alpha = 237.4$ cc/kg | | |
| Model | $T$ K | $-\Delta H_0$ | $\frac{-\Delta H_0}{RT_C}$ | $\frac{-\Delta S}{R}$ | $-\Delta H_0$ | $\frac{-\Delta H_0}{RT_C}$ | $\frac{-\Delta S}{R}$ |
| RL | 298 | 41.12 | 7.64 | −8.76 | 55.16 | 10.25 | 5.21 |
| TT | 298 | 50.66 | 9.42 | −3.81 | 56.38 | 10.48 | 5.78 |
| TL | 298 | 43.39 | 8.07 | −5.91 | 56.38 | 10.48 | 5.50 |
| LL | 298 | 33.01 | 6.14 | −8.60 | 55.31 | 10.28 | 5.80 |
| Morris | 298 | 36.11 | 6.71 | | | | |
| Using calorimetric heat of sorption for the $\beta$ cage | | | | | | | |
| RL | 298 | 102.5 | 19.9 | 16.02 | | | |
| TT | 298 | 102.5 | 19.9 | 20.97 | | | |
| TL | 298 | 102.5 | 19.9 | 18.86 | | | |
| LL | 298 | 102.5 | 19.9 | 16.18 | | | |
| Morris | 298 | 102.5 | 19.9 | | | | |
| LL | 334 | 102.5 | 19.9 | 13.40 | | | |
| LL | 378 | 102.5 | 19.9 | 10.70 | | | |
| (b) ZSM-22(TON) | | $V_P = 69$ cc/kg | | | | | |
| $C_2H_6$ | 310 | 39 | 15.4 | 6.6 | | | |
| $n$-$C_8H_{18}$ | 523 | 100.6 | 21.3 | 16.8 | | | |
| (c) Faujasite | | | | | $V_P = 320$ cc/kg | | |
| Gas | | | | | | | |
| $O_2$ | 306.31 | | | | 15.0 | 11.7 | 3.8 |
| $C_2H_6$ | 293.15 | | | | 26.9 | 10.6 | 4 |
| Polar molecules | | | | | | | |
| $N_2$ | 305.62 | | | | 19.9 | 19.0 | 4.4 |
| $C_2H_4$ | 293.15 | | | | 41.8 | 17.8 | 6.6 |

a large molecule in a small pore whereas water is a relatively small molecule in a similar size pore. If we examine a small molecule such as ethane in ZSM-5 we observe that the standard enthalpy of sorption, the dimensionless standard enthalpy of sorption and the dimensionless entropy of sorption are all much reduced. In fact the dimensionless entropy of sorption for ethane is 6.6 in ZSM-5, much less than $n$-octane. However, the dimensionless entropy of sorption of water reduces from 16.18 to 10.70 as the temperature increases from 298 to 378 suggesting that water is transiting from a large molecule to a small molecule with rise in temperature. Is this feasible?

A review of the properties of water reveals that there are 12 different phases of ice, and that water itself may exist as clusters of dimers or trimers. Other possibilitiesare water of hydrate formation or water clathrate formation within the cavity. These possibilities may be responsible for the dimensionless differential entropy changes observed. There is some evidence that this may be happening. Dubinin and coworkers report that in some cases the adsorption of water is in the form of ice. Further, his group observed a doublet presumably a dimer when making infra-red spectroscopic measurements (Dubinin et al. 1975) and observed clusters of water in another study (Glazun et al. 1967). Hino (1977) also observed another water species present in the zeolite. The formation of the various ice phases needs very high pressure which is exactly the conditions adsorption provides in the $\beta$ cage.

The $\beta$ cage adsorbs 5 molecules of water providing a site for the formation of a cyclic pentamers. The cyclic pentamer unravels to the linear pentamer between 400 and 425 K. Breck (3) indicates that there are occlusions of NaAlO subscript 2 in the beta cage. This amy imply it is a combination of contaminants and the water which is causing the problem.It will be interesting to see if the other A type zeolites exhibit the same phenomenom.

The adsorption of water in the $\alpha$ cage is compared to the adsorption of non-polar and polar molecules in faujasite in Table 6. The volume of 4A $\alpha$ cage is 237.4 cc/kg and that of faujasite is 320 cc/kg. Note, the cavity volume of faujasite of 320 cc/kg probably represents the sum of the $\beta$ cage and large cavity, so that a true comparison may be between the large cavity of 274 cc/kg in faujasite and the $\alpha$ cage. The standard total enthalpy of water in the $\alpha$ cage is greater than any polar or non-polar molecules in the data of Myers (2004). However, the dimensionless standard enthalpy of sorption is similar to that for the non-polar gases and 60 per cent of that for the polar gases. The 60% figure is a surprise as it is consistent with just dispersion forces as reported by Myers (2004) implying limited electrostatic energy forces in the large cavity for water. The dimensionless entropy of sorption is very similar to the polar gases. However, these values are not much greater than the non-polar gases.

To use the Langmuir-Langmuir model predictively, the incremental change in $\Delta S/R$ versus inverse temperature is

$$\frac{\Delta S}{R} = \frac{7715.9}{T} - 9.7088 \tag{32}$$

Surprisingly the $R^2$ value for this equation is 0.9999. The author expected some curvature tapering to an asymptotic value greater than that for the $\alpha$ cage. More data is required to establish extrapolated information outside the temperature region for which it was derived. The general equations for $K_\alpha$ and $K_\beta$ are

$$K = e^{\Delta S/R} e^{-\Delta H/RT} \tag{33}$$

For $K_\beta$

$$\begin{aligned} &\frac{\Delta S}{R} = \frac{7715.9}{T} - 9.7088 \quad \text{and} \\ &-\Delta H = 102.5 \text{ kJ/mol} \end{aligned} \tag{34}$$

For $K_\alpha$

$$\frac{\Delta S}{R} = -5.57 \quad \text{and} \quad -\Delta H = 55.80 \text{ kJ/mol} \tag{35}$$

To calculate the equilibrium parameters $K_1$ and $K_2$, $K_\alpha$ and $K_\beta$ must be pre-multiplied by:

$$K_{1 \text{ or } 2} \text{ in mbar}^{-1} = \frac{\omega M W_{H_2O} V_p}{R T \rho_z V_z q_s} K_{\alpha \text{ or } \beta} \tag{36}$$

$$K_{1 \text{ or } 2} \text{ in mbar}^{-1} = \frac{4.599\text{E-}05}{T} K_{\alpha \text{ or } \beta} \tag{37}$$

## 5 Conclusions

The adsorption data of Gorbach et al. (2004) and Morris (1968) for the adsorption of water on 4A zeolite has been re-analyzed. Model isotherms have been derived considering a two site hypothesis, one for the $\alpha$ cage and one for the $\beta$ cage. 4 simple model isotherms were fitted to the data. Fitting the data with Henry's Law reveals that in the $\beta$ cage region, the Gorbach et al. (2004) data is heterogeneous whereas the Morris (1968) data is homogeneous. The model best representing the Gorbach et al. (2004) data involved employing a Toth isotherm on each site whereas the Morris (1968) data was easily fitted with a two site Langmuir isotherm. As the dual site Langmuir isotherm fits both data sets reasonably, it is recommended.

Analysis of the equilibrium Henry law fits in terms of a dimensionless equilibrium constant $K_C$ and its intrinsic enthalpy and entropy of adsorption parameters, reveals satisfactory regression results for the $\alpha$ cage but surprising results for the $\beta$ cage. The enthalpy of the $\beta$ cage is $1/3$rd of that observed calorimetrically, and the standard entropy of adsorption is positive, a physical impossibility. Substituting the calorimetric enthalpy of adsorption corrected the standard differential entropy of sorption values but these values were found to vary significantly with temperature. The variation was postulated to be due to the formation of clusters of water.

The simple two site model proposed in this study can be used for other zeolites in which adsorption occurs in both a $\beta$ cage and an $\alpha$ cage such as the adsorption of ammonia or water in 3A, 4A, 5A, 10X, 13X, and faujasite X or Y zeolites to list just a few.

**Acknowledgements** The author wishes to acknowledge the support of the American University of Sharjah for a seed grant for the execution of this study.

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