

Statistical Thermodynamics of Methanol and Ethanol Adsorption in Zeolite NaZSM5

B. Boddenberg,^{*,†} G. U. Rakhmatkariev,[‡] and R. Greth[†]

Lehrstuhl für Physikalische Chemie II, University Dortmund, D-44221 Dortmund, Germany, and
Institute of Chemistry, Academy of Sciences, 700170 Tashkent, Uzbekistan

Received: October 9, 1996; In Final Form: December 29, 1996[®]

A statistical thermodynamic treatment of the adsorption of methanol and ethanol in zeolite NaZSM5 at 303 K is presented that reproduces well the adsorption isotherm and differential heat of adsorption data published by M. M. Dubinin, G. U. Rakhmatkariev, and A. A. Isirikyan (*Izv. Akad. Nauk SSSR, Ser. Khim.* **1989**, 11, 2636). The pore filling proceeds via the formation of monomeric up to tetrameric alcohol/cation complexes located in the channel intersections. The equilibrium concentrations of these s -meric complexes ($s = 1-4$) as a function of the overall loading as well as the potential energies and energies of formation of the complexes are determined.

1. Introduction

The adsorption of short-chain aliphatic alcohols like methanol and ethanol in the channel system of the pentasil type zeolites silicalite, HZSM5, and NaZSM5 has repeatedly been studied by a variety of classical thermodynamic and spectroscopic techniques.¹⁻¹² Most of these papers¹⁻¹¹ were focused on studies with the former two zeolites because of their application as materials for removing organic substances from aqueous phases (silicalite)¹³ and as catalysts for the methanol to gasoline conversion process (HZSM5).¹⁴ Repeatedly, it has been realized that even small amounts of Na⁺ ions in such zeolites lead to enhanced adsorption.¹⁵ In their studies of methanol and ethanol in NaZSM5, Dubinin et al.¹² have detected not only enhanced adsorption but also dramatic changes of the shapes of the adsorption isotherms and the differential heat vs loading curves. Their interpretation of these findings, that monomeric up to tetrameric alcohol/cation complexes are successively formed in the intersections of the system of parallel straight and zigzag channels of this zeolite, is analyzed in the present work by means of statistical thermodynamic considerations.

2. Basic Relationships of Statistical Thermodynamics

Consider a collection of M independent equivalent sites on each of which any number s , from zero to a maximum m , of identical molecules can be attached. In terms of the grand canonical partition function $\Xi(M, T, \mu)$ where μ is the chemical potential of the bound species, the total number N and the energy E of the system are given by¹⁶

$$N = kT \left(\frac{\partial \ln \Xi}{\partial \mu} \right)_{M, T} \quad (1a)$$

and

$$E = kT^2 \left(\frac{\partial \ln \Xi}{\partial T} \right)_{M, \mu} + N\mu \quad (1b)$$

If the molecule/site complexes are noninteracting, the partition function Ξ can be factorized¹⁶ according to

$$\Xi(M, T, \mu) = \xi(T, \lambda)^M \quad (2a)$$

where

$$\xi(T, \lambda) = \sum_{s=0}^m q_s(T) \lambda^s \quad (2b)$$

is the grand canonical partition function referred to a single site, $q_s(T)$ is the partition function of a site with s bound molecules, and $\lambda = \exp(\mu/kT)$ is the absolute activity.

Inserting eqs 2a,b into eqs 1a,b and applying some straightforward mathematical operations, the following relationships are obtained:

$$\frac{N}{M} = \frac{(\sum_{s=0}^m s q_s \lambda^s)}{(\sum_{s=0}^m q_s \lambda^s)} \quad (3a)$$

and

$$E = NkT^2 \frac{(\sum_{s=0}^m q'_s \lambda^s)}{(\sum_{s=0}^m s q_s \lambda^s)} \quad (3b)$$

In eq 3b $q'_s = dq_s/dT$.

In adsorption equilibrium with the gas phase, which is assumed to behave ideally, the chemical potential μ can be expressed as

$$\mu = \mu^0(T) + kT \ln(p/p^0) \quad (4a)$$

where $\mu^0(T)$ is the chemical potential of the adsorptive at the liquid/vapor equilibrium at temperature T , p^0 is the vapor pressure, and p is the pressure at the sorbate/gas equilibrium. In terms of the absolute activity eq 4a may be rewritten in the form

$$\lambda = \lambda_0 x \quad (4b)$$

where $x = p/p^0$ is the relative pressure, and $\lambda_0 = \exp(\mu^0/kT)$.

Introducing eq 4b in eqs 3a and 3b, we obtain the thermodynamic quantities N and E as a function of x , i.e. as a function of relative pressure. So, eq 3a yields the adsorption isotherm in familiar form,

$$y \equiv \frac{N}{M} = \frac{(\sum_{s=0}^m s c_s x^s)}{(\sum_{s=0}^m c_s x^s)} \quad (5a)$$

with

[†] University Dortmund.

[‡] Institute of Chemistry, Uzbekistan.

[®] Abstract published in *Advance ACS Abstracts*, February 1, 1997.

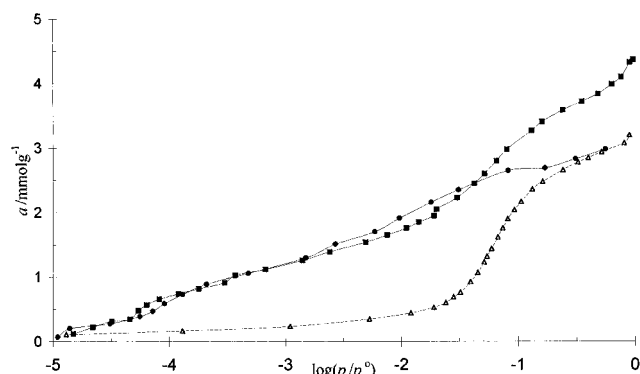


Figure 1. Adsorption isotherms (303 K) of methanol in NaZSM (■)¹² and silicalite (△)⁹ and of ethanol in NaZSM5 (●).¹²

$$c_s = q_s \lambda_0^s \quad (5b)$$

By definition, the differential heat of adsorption Q_d is¹⁷

$$Q_d = E^g - N_A \left(\frac{\partial E}{\partial N} \right)_{M,T} \quad (6a)$$

with

$$E^g = RT^2 \ln q^g/dT \quad (6b)$$

In these equations E^g is the molar energy of the gas, q^g is the partition function of a molecule in the gas phase, and N_A is Avogadro's constant. Introducing eqs 3b and 4b, the differential heat of adsorption is obtained in the following convenient form:

$$Q_d = E^g - \frac{\partial}{\partial y} \left[y \left(\sum_{s=0}^m c_s E_s x^s \right) / \left(\sum_{s=0}^m s c_s x^s \right) \right]_{M,T} \quad (7a)$$

where

$$E_s = RT^2 \ln q_s/dT \quad (7b)$$

is the molar energy of a site with s bound molecules. In the square bracket term of eq 7a x is expressed as a function of y ; that is, $x(y)$ is the inverse function of the adsorption isotherm.

3. Methanol and Ethanol in NaZSM5

3.1. Experimental Data. Dubinin and co-workers¹² have measured the adsorption isotherms and differential heats of adsorption, Q_d , of methanol and ethanol at 303 K in zeolite NaZSM5, Si/Al = 32, which was evacuated for 10 h at 450 °C prior to admission of the sorbates. Their data are reproduced in Figures 1 and 2 together with the adsorption isotherm and the differential heats of adsorption of methanol in silicalite.⁹ The adsorption isotherms of both alcohols in NaZSM5 exhibit undulatory shapes and saturation capacities of about 3.8 (CH₃-OH) and 3.1 (C₂H₅OH) mmol/g. In silicalite, the adsorption isotherm of methanol sets in at considerably higher pressure and exhibits a sigmoid shape with saturation capacity of about 3.2 mmol/g.

The differential heats of adsorption of the alcohols in NaZSM5 initially decrease steeply with increasing degree of pore filling and subsequently decrease in steps, whereas in silicalite the initial decrease is followed by a continuous increase up to loadings near saturation.

The drastic differences between NaZSM5 and silicalite that show up in the figures, indicate that in the former case the interaction of the molecules with the extralattice cations plays a dominant role. Dubinin et al.¹² have suggested that by the

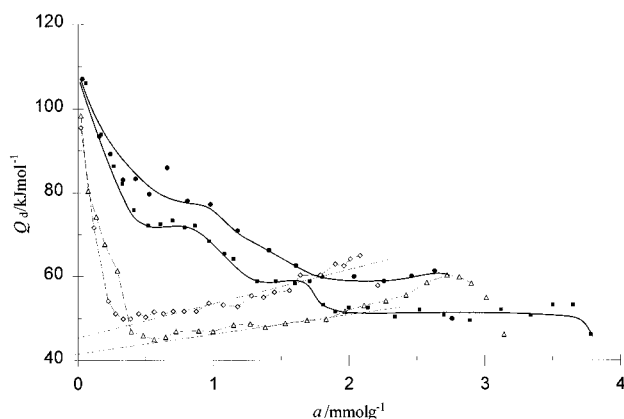


Figure 2. Differential heat of adsorption, Q_d , of methanol in NaZSM5 (■)¹² and silicalite (△)⁹ and of ethanol in NaZSM5 (●).¹²

initial admission of the alcohols the cations are displaced from their wall positions into the channel intersections and here successively monomeric up to tetrameric molecule/cation complexes are formed. According to the sodium content of the studied zeolite, the complete complexation to tetrahedral-like entities is attained at 2 mmol/g, beyond which loading the further adsorption was attributed to filling of the residual cation-free pore volume. Actually, methanol adsorption in silicalite whose surface properties should be similar to the cation-free regions of NaZSM5, sets in at about $p/p^0 = 0.01$ (Figure 1) where the adsorption in NaZSM5 is already close to 2 mmol/g. So, up to this pressure the alcohol/cation system can fairly be assumed to remain undisturbed by the further incorporation of the alcohols in the pore system.

3.2. Adsorption Isotherms. Following closely the proposal of Dubinin et al.,¹² it is assumed that alcohol/cation complexes, (Alc)_sNa⁺ ($s = 0, \dots, 4$), involving each of the sodium ions available, are formed in the channel intersections, and thermodynamic equilibrium is established. Since the channel intersections are well separated from each other, mutual interaction of the complexes can be neglected. Under these circumstances, the premises of the statistical mechanical model of the previous section are well fulfilled.

With a maximum of $m = 4$ alcohol molecules attached to each sodium cation, the general adsorption isotherm equation, eq 5a, simplifies to

$$\frac{N}{M} = \frac{c_1 x + 2c_2 x^2 + 3c_3 x^3 + 4c_4 x^4}{1 + c_1 x + c_2 x^2 + c_3 x^3 + c_4 x^4} \quad (8)$$

where $x = p/p^0$ is the relative pressure. With the known chemical composition of the zeolite under study, the transcription of the adsorbed amount a (Figure 1) into N/M is $N/M = 2.0 a/\text{mmol g}^{-1}$. Actually, in this zeolite there are three Na⁺ per unit cell; that is, three Na⁺ ions are available per four channel intersections.

The adsorption isotherms of methanol and ethanol fitted with eq 8 are shown in Figures 3 and 4, respectively, both displayed on a linear pressure scale covering the range of pore filling up to 4 molecules/Na⁺ and on a logarithmic pressure scale covering the complete pressure range investigated. The values of the best fit parameters c_1 – c_4 are collected in Table 1. Obviously, the experimental data up to $N/M = 4$ can very well be reproduced, lending support for the appropriateness of the underlying model.

For the purpose of later application, Table 1 contains also the partition functions of the s -meric complexes calculated from the parameters c_s according to eq 5b. The standard activity λ_0

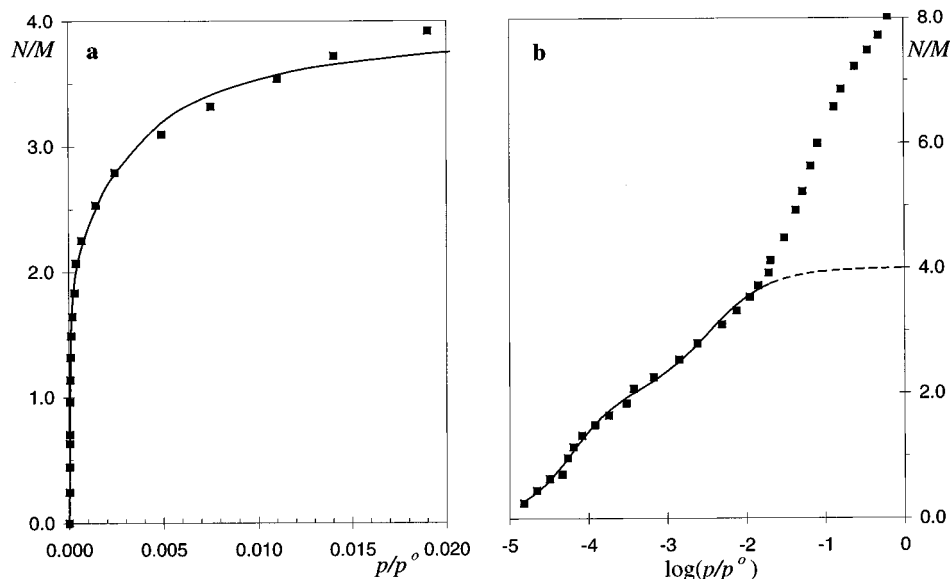


Figure 3. Adsorption isotherm (303 K) of methanol in NaZSM5 on linear (a) and logarithmic (b) relative pressure scales. The solid curves are fits as discussed in the text.

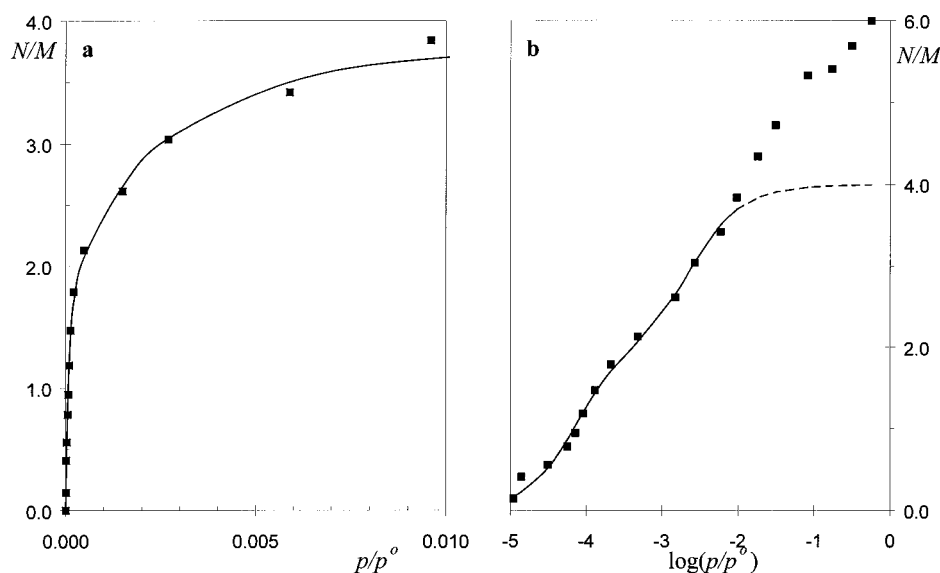


Figure 4. Adsorption isotherm (303 K) of ethanol in NaZSM5 on linear (a) and logarithmic (b) pressure scales. The solid curves are fits as discussed in the text.

TABLE 1: Coefficients c_s of Isotherm Equation and Partition Functions q_s of s -Mers of Methanol and Ethanol in Zeolite NaZSM5

	CH ₃ OH	C ₂ H ₅ OH
c_1	1.48×10^4	1.46×10^4
q_1	2.4×10^{15}	3.2×10^{17}
c_2	2.84×10^8	2.01×10^8
q_2	7.7×10^{30}	9.5×10^{34}
c_3	1.25×10^{11}	9.14×10^{10}
q_3	5.6×10^{44}	9.4×10^{50}
c_4	2.36×10^{13}	3.35×10^{13}
q_4	1.7×10^{58}	7.5×10^{66}

needed for this calculation is¹⁶

$$\lambda_0 = \frac{N}{q^0} \quad (9a)$$

where q^0 is the partition function of a molecule in the gas phase at liquid/vapor equilibrium. This partition function was calculated according to the standard formula¹⁶

$$\frac{q^0}{N} = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{kT}{p^0} q_{\text{rot}} q_{\text{vib}} \quad (9b)$$

where q_{rot} and q_{vib} are the rotational and vibrational partition functions, respectively. From tabulated thermodynamic data¹⁸ the vapor pressures at 303 K were calculated to be $p^0(\text{CH}_3\text{OH}) = 207$ hPa and $p^0(\text{C}_2\text{H}_5\text{OH}) = 100$ hPa. q_{rot} and q_{vib} for methanol were calculated from molecular data and tabulated normal mode frequencies.¹⁹ Quantum chemical calculations yielded somewhat different frequencies but practically the same values of q_{vib} . The partition functions for ethanol were obtained from normal mode frequencies calculated quantum mechanically and tabulated standard entropies.²⁰ The values of the vibrational partition functions of methanol and ethanol (energy zero is the lowest energy level) and of the quantities derived therefrom, namely, the vibrational energies E_{vib} and the absolute activities λ_0 , are collected in Table 2.

3.3. Differential Heats of Adsorption. The analysis of the experimental differential heats of adsorption of methanol and ethanol in NaZSM5 (Figure 2) is based on eq 7a. This requires

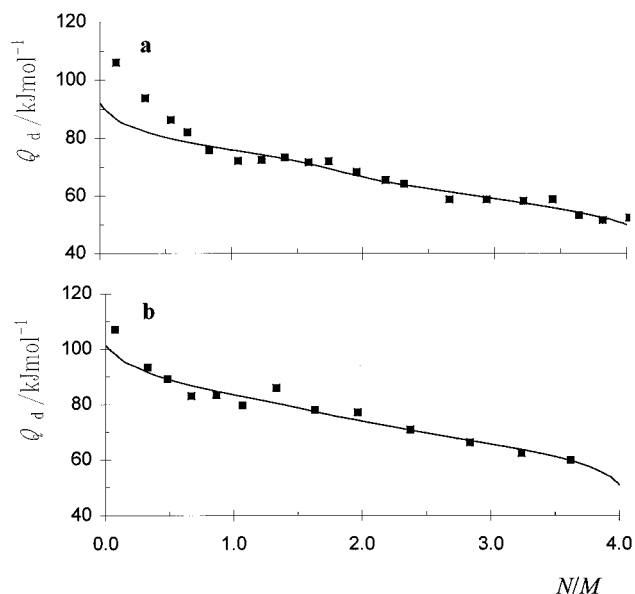


Figure 5. Differential heats of adsorption of methanol (a) and ethanol (b) in NaZSM5. The solid curves are fits as discussed in the text.

TABLE 2: Statistical Thermodynamic Data of Methanol and Ethanol in the Gas Phase, $T = 303$ K

	CH ₃ OH	C ₂ H ₅ OH
q_{vib}	1.42	2.7
$E_{\text{vib}}/\text{kJmol}^{-1}$	1.34	4.3
λ_0	6.1×10^{-12}	4.6×10^{-14}

TABLE 3: Energy Data (in kJ mol⁻¹) of the s -Meric Complexes of Methanol and Ethanol in Zeolite NaZSM5

s	methanol			ethanol		
	E_s (E_s/s)	$\Delta_f E_s$ ($\Delta_f E_s/s$)	U_s^0 (U_s^0/s)	E_s (E_s/s)	$\Delta_f E_s$ ($\Delta_f E_s/s$)	U_s^0 (U_s^0/s)
1	-83 (-83)	-92 (-92)	-96 (-86)	-89 (-89)	-101 (-101)	-98 (-98)
2	-134 (-67)	-143 (-72)	-154 (-77)	-142 (-71)	-166 (-83)	-173 (-87)
3	-193 (-64)	-202 (-67)	-224 (-75)	-210 (-70)	-246 (-82)	-255 (-85)
4	-234 (-59)	-243 (-61)	-285 (-71)	-249 (-62)	-297 (-74)	-314 (-79)

the determination of the molar energy of the gas, E_s^g , and of the energies of the s -meric complexes, E_s . Using the vibrational energies from Table 2, the former quantities are readily calculated to be $E_s^g(\text{CH}_3\text{OH}) = 8.9 \text{ kJ mol}^{-1}$ and $E_s^g(\text{C}_2\text{H}_5\text{OH}) = 11.9 \text{ kJ mol}^{-1}$. The quantities E_s are treated as fit parameters.

Figure 5 shows the fit curves through the experimental heats of adsorption of both methanol and ethanol obtained with the values of E_s collected in Table 3. Besides some deviations at low loadings, which are more pronounced in the case of methanol, the experimental heat data are rather well reproduced. Several reasons can be imagined to cause the initial discrepancies. First, there may exist some amount of structural OH-groups, which are known to represent strong adsorption centers for alcohols.^{1,5,21} Actually, the strong initial rises of the differential heats of adsorption of alcohols in silicalite as in the case of methanol (Figure 2) have been attributed to such centers.²¹ Second, it can readily be imagined that the monomeric alcohol/cation species remain located at different positions of the zeolite framework, entailing some distribution of the monomer energy E_1 . It is recalled that the model on which the present analysis is based assumes displacement of the cations into energetically equivalent positions in the channel intersections. This notion could explain the greater deviations in the

case of methanol because this small molecule ($\varnothing 0.4 \text{ nm}$) should be able to associate well with a cation remaining sited on a channel wall, whereas in the case of ethanol the energetically most favored location of the monomer is in the channel intersection. It should be stressed that the described effect does not violate the basic presumptions of the model because the exact location of the monomeric complex is immaterial for its validity. On the other hand, the statistical thermodynamic relationships formulated previously and used throughout do not account for the discussed energetic inhomogeneities.

4. Discussion

4.1. Site Occupancies and Distribution of the Alcohol Molecules. At any concentration N/M ($0 \leq N/M \leq 4$) the alcohol molecules are expected to exhibit some well-defined distribution over the various s -meric complexes in the channel intersections. The relevant measures are the fraction of sites carrying s attached molecules (p_s) and the fraction of molecules in each kind of s -mers (f_s), which can be calculated according to¹⁶

$$p_s = \frac{c_s x^s}{\xi} \quad (10a)$$

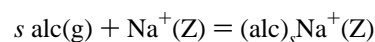
and

$$f_s = \frac{s c_s x^s}{\sum_{s=0}^4 s c_s x^s} \quad (10b)$$

where $\xi = 1 + c_1 x + \dots + c_4 x^4$ is the grand canonical partition function per site (see eq 2b). These fractions, calculated with the known values of the coefficients c_s (Table 1), are shown in Figures 6 and 7 as a function of N/M for methanol and ethanol, respectively. As is expected, the fractions of empty sites, p_0 , and of the tetramers, p_4 , monotonously decrease and increase with N/M , respectively, whereas the fractions of monomers, dimers, and trimers each run through a maximum located at about $N/M = 1, 2$, and 3 , respectively. In comparison to the strictly successive formation of the s -mers proposed by Dubinin et al.¹² (dashed curves in Figure 6), the present treatment predicts more washed-out features with at least four of the five types of sites being present to an appreciable extent at each loading N/M ($N/M < 4$). So, the basic idea of Dubinin et al. still holds true but experiences modification and quantitative formulation by the present treatment.

Referring to Figures 6 and 7, two peculiarities are noted that are of importance for the later discussion. In the zero-loading limit ($N/M \rightarrow 0$), the only species formed from the empty sites are the monomers, and in the high-loading limit ($N/M \rightarrow 4$) the tetramers are exclusively formed from the trimers.

4.2. Energies of Formation of the Alcohol/Cation Complexes. The energies of the s -meric complexes, E_s , are defined relative to the lowest energy gas state, and so are quantities that escape comparison with any value of the measured differential heats of adsorption. Therefore, we define the energy of formation of an s -meric alcohol (alc)/sodium cation complex in the zeolite (Z), $\Delta_f E_s$, to be the molar energy change associated with the stoichiometric equation



so that

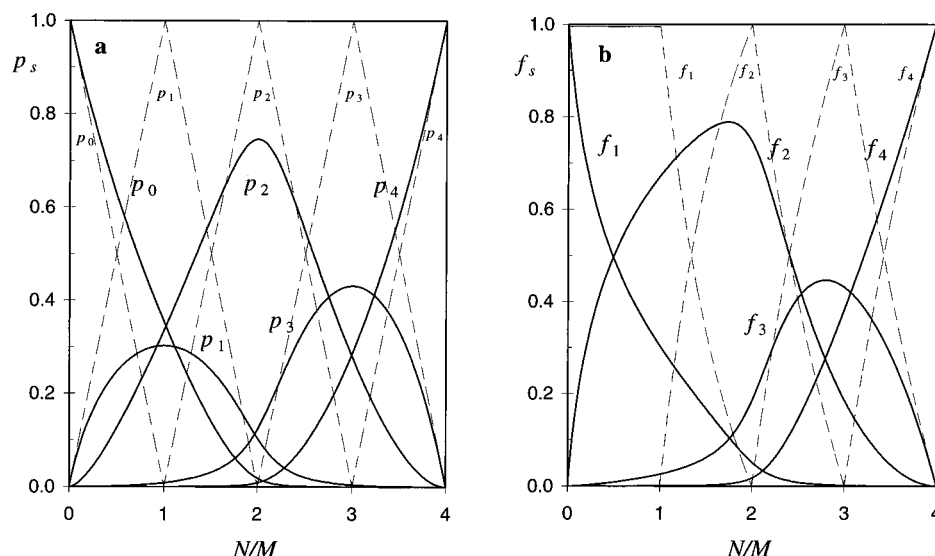


Figure 6. Fraction of *s*-meric methanol complexes (a) and fraction of methanol molecules contained in *s*-mers (b) in zeolite NaZSM5 as a function of overall concentration N/M . The dashed lines correspond to strictly successive formation of the *s*-mers.

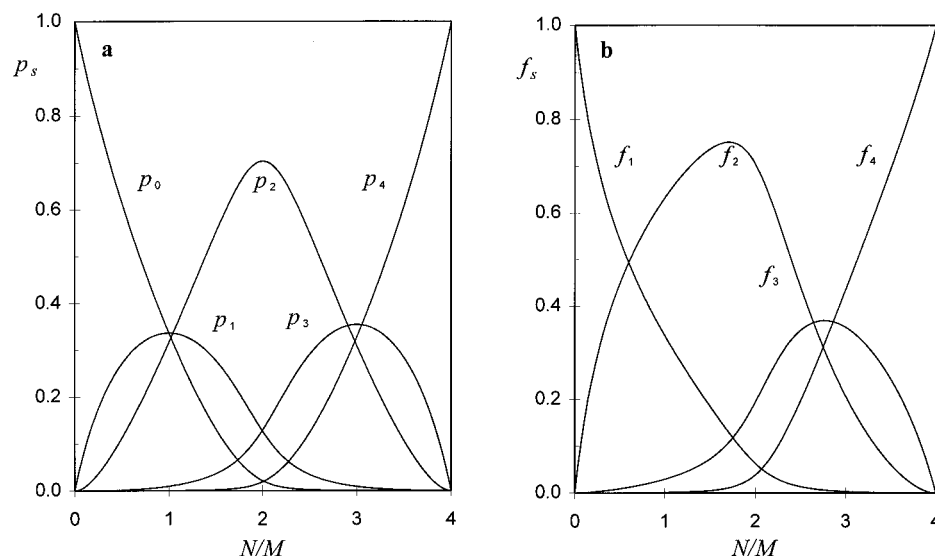


Figure 7. Fraction of *s*-meric ethanol complexes (a) and fraction of ethanol molecules contained in *s*-mers (b) in zeolite NaZSM5 as a function of overall concentration.

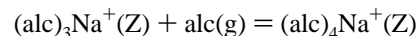
$$\Delta_f E_s = E_s - sE^g \quad (11)$$

With the previously cited values of E^g and E_s from Tables 2 and 3, we readily obtain the energies of formation collected in columns 3 and 6 of Table 3.

The energy of formation of the monomers, $\Delta_f E_1$, is identical to the negative value of Q_d at vanishing loading ($\Delta_f E_1 = -Q_d$ ($N/M \rightarrow 0$)) because in this limit the monomers are the only species formed from the empty sites (vide supra). Since Q_d is a differential quantity, no further energy of formation can be associated with some value of the Q_d vs N/M curve.

It is interesting to inquire the meaning of Q_d in the high-loading limit ($N/M \rightarrow 4$). From Figure 5 $Q_d(N/M \rightarrow 4) = 50$ and 51 kJ mol^{-1} is obtained for methanol and ethanol, respectively. Without thorough reflection, one might guess that these values are to be identified with the negative of the energies of formation of the tetramers referred to one alcohol molecule. Inspection of Table 3 reveals, however, that the values of the latter quantities are 61 kJ mol^{-1} (CH_3OH) and 74 kJ mol^{-1} ($\text{C}_2\text{H}_5\text{OH}$), and so are much different from the high-loading limits of Q_d . Actually, in this limit the tetramers are exclusively formed from the trimers (vide supra), and so here Q_d should be

identical with the energy change associated with the reaction



with

$$\Delta_f E = E_4 - E_3 - E^g$$

Alternatively, $\Delta_f E$ may be obtained from the equation

$$\Delta_f E = \Delta_f E_4 - \Delta_f E_3$$

Using the data of Table 3, it is easy to prove that the relation $-\Delta_f E = Q_d(N/M \rightarrow 4)$, in fact, holds true.

Most certainly, the ligand alcohol molecules are oriented with the polar alcoholic group next to the cation. So, it is of interest to have available an estimate of the alcohol to cation bonding energy, which besides van der Waals type and thermal contributions is part of the energy of formation per molecule, $\Delta_f E_s/s$. For a rough estimate, we compare $-\Delta_f E_1$ of methanol and ethanol with the initial heats of adsorption Q_d of these alcohols in silicalite. This initial heat, $Q_d(a \rightarrow 0)$, is here defined to be the ordinate intersection of the medium-loading straight line of

the Q_d vs a curve (see Figure 2). These values are $Q_d(a \rightarrow 0) = 43 \text{ kJ mol}^{-1}$ for methanol from Figure 2 and likewise from the data published by Thamm,⁵ and $Q_d(a \rightarrow 0) = 51 \text{ kJ mol}^{-1}$ for ethanol, being the average of the values 53 and 49 kJ mol^{-1} extracted from the work of Dubinin et al.⁶ and Thamm,⁵ respectively. The difference of $Q_d(a \rightarrow 0)$ for silicalite against the corresponding $-\Delta_f E_1$ for NaZSM5 (Table 3) is 50 kJ mol^{-1} for both alcohols. Following the reasoning pursued so far, this energy is expected to be close to the energy of the attachment of one molecule of either methanol or ethanol to a sodium cation.

4.3. Potential Energies of the Alcohol/Cation Complexes.

The potential energy of an s -meric alcohol/cation complex in the zeolite matrix, U_s^0 , is defined to be the energy of the lowest state of the complex with zero gas phase energy. Accordingly, we have the relation

$$U_s^0 = E_s - E_s^{\text{th}} \quad (12)$$

where E_s^{th} is the thermal energy of the complex, i.e. the energy of the s -mer relative to its lowest energy state. Likewise, the partition functions q_s can be written as

$$q_s = \bar{q}_s e^{-U_s^0/RT} \quad (13)$$

where \bar{q}_s is the partition function with energy zero at the lowest energy of the complex. Unfortunately, spectroscopic data of the complexes are not available, which prevents the calculation \bar{q}_s and, hence, the determination of U_s^0 .

To proceed, we introduce, heuristically, some simplified model that may account reasonably well for the motional state of the complexes. The relevant assumptions are as follows. (i) The complexes are exclusively determined by vibrational degrees of freedom. (ii) The normal mode vibrations of the complexes can be separated into internal modes of the molecules, like in the gaseous state, and external modes describing the vibrations relative to the cation and the matrix. (iii) The 6s external vibrational modes of each s -mer all exhibit the same frequency. With these assumptions the partition function \bar{q}_s of an s -meric complex is

$$\bar{q}_s = q_{\text{int}}^s (q_{\text{ext}})^{6s} \quad (14)$$

where q_{int} denotes the partition function of the internal vibrational modes per molecule (identical with q_{vib} of Table 2), and q_{ext} is the partition function per external vibrational mode. Noting that $E_s^{\text{th}} = RT^2 \ln \bar{q}_s / dT$, we obtain with eq 14

$$E_s^{\text{th}} = sE_{\text{int}} + 6sRT^2 \ln q_{\text{ext}} / dT \quad (15a)$$

where E_{int} is the energy of the internal vibrations (identical with E_{vib} of Table 2). Again with eq 14, the partition function q_s according to eq 13 may be reformulated as

$$\ln q_s = s \ln q_{\text{int}} + 6s \ln q_{\text{ext}} - \frac{U_s^0}{RT} \quad (15b)$$

Putting together eqs 12, 15a, and 15b the following relationship is obtained.

$$6s(\ln q_{\text{ext}} + T \ln q_{\text{ext}} / dT) = \frac{E_s - sE_{\text{int}} + RT \ln(q_s / q_{\text{int}}^s)}{RT} \quad (16)$$

The right-hand side of this equation contains quantities that are known from the analysis of the experiments (E_s , q_s) or from

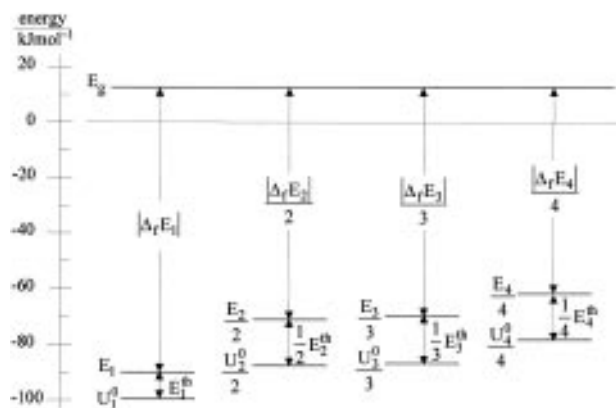


Figure 8. Energies of the s -meric ethanol/sodium cation complexes in zeolite NaZSM5.

previous calculations (E_{int} , q_{int}). On the other hand, the left-hand side contains the unknown partition function q_{ext} and the derivative with respect to temperature. Since the analytical form of the vibrational partition function is well-known,¹⁶ we can determine the vibrational frequency ν by a simple iteration procedure. With known frequency, we then can easily calculate \bar{q}_s (eq 14) and determine U_s^0 (eq 13). The obtained frequencies for the methanol and ethanol s -mers are in the ranges $(1.3-1.5) \times 10^{13} \text{ s}^{-1}$ for the monomers and $(3-5) \times 10^{12} \text{ s}^{-1}$ for the dimers, trimers, and tetramers. These figures are considered to be of very reasonable magnitude. The potential energy data evaluated are collected in Table 3. Figure 8 displays the energetic data of the s -mers of ethanol in zeolite NaZSM5 in form of an energy ladder diagram.

As is expected, the potential energy per ligand molecule, U_s^0/s , increases (its modulus decreases) with increasing number of molecules attached to the cation in the cases of both methanol and ethanol. Systematically, the potential energy values for ethanol are lower by about 10 kJ mol^{-1} in comparison to methanol, which may, probably, be due to the differences between the van der Waals interaction energies of the alcohols with the cation and the framework. Certainly, it is an interesting task to confirm the obtained energy values by quantum chemical calculations.

5. Conclusions

Thermodynamic data of the adsorption of methanol and ethanol in zeolite NaZSM5 (adsorption isotherms and differential heats of adsorption) have been shown to be accessible to a quantitative treatment using statistical thermodynamic concepts. The results indicate that due to the strong specific interaction of the alcohol molecules with the cations, monomeric up to tetrameric complexes are formed in the channel intersections of this zeolite. It is expected that the adsorption of molecules capable of specific interactions with the extraframework cations in this type of zeolite can be treated with concepts similar to those used presently.

Acknowledgment. This work was performed within the program of scientific exchange between Germany and the Republic of Uzbekistan. Thanks are due to Prof. Dr. P. Bleckmann and Dipl. Chem. F. Rittner for performing the normal mode analysis of the alcohols.

References and Notes

- (1) Pope, C. G. *J. Chem. Soc., Faraday Trans.* **1993**, 89, 1139.
- (2) Pelmenchikov, A. G.; Morosi, G.; Gamba, A.; Zecchina, A.; Bordiga, S.; Paukshits, E. A. *J. Phys. Chem.* **1993**, 97, 11979.

- (3) Anderson, M. W.; Barrie, P. J.; Klinowski, J. *J. Phys. Chem.* **1991**, 95, 235.
- (4) Mirth, G.; Lercher, J. A.; Anderson, M. W.; Klinowski, J. *J. Chem. Soc., Faraday Trans.* **1990**, 86, 3039.
- (5) Thamm, H. *J. Chem. Soc., Faraday Trans.* **1989**, 85, 1.
- (6) Dubinin, M. M.; Rakhmatkariev, G. U.; Isirikyan, A. A. *Izv. AN SSSR, Ser. Khim.* **1989**, 9, 2117.
- (7) Aronson, T.; Gorte, R. J.; Farneth, W. A.; White, D. *Langmuir* **1988**, 4, 702.
- (8) Sass, C. E.; Kevan, L. *J. Phys. Chem.* **1988**, 92, 5192.
- (9) Akhmedov, K. S.; Rakhmatkariev, G. U.; Dubinin, M. M.; Isirikyan, A. A. *Izv. AN SSSR, Ser. Khim.* **1987**, 8, 1717.
- (10) Jobic, H.; Renouprez, A.; Bec, M.; Poinsegon, C. *J. Phys. Chem.* **1986**, 90, 1059.
- (11) Narasimhan, C. S.; Narayana, M.; Kevan, L. *J. Phys. Chem.* **1983**, 87, 984.
- (12) Dubinin, M. M.; Rakhmatkariev, G. U.; Isirikyan, A. A. *Izv. AN SSSR, Ser. Khim.* **1989**, 11, 2636.
- (13) Meisel, S. J.; Mc Cullough, J. P.; Lechthaler, C. H.; Weisz, P. B. *CHEMTECH* **1976**, 6, 86.
- (14) Flanigen, E. M.; Bennett, J. M.; Grose, R. W.; Cohen, J. P.; Patton, R. L.; Kirchner, R. M.; Smith, J. V. *Nature* **1978**, 271, 512.
- (15) Matsumura, Y.; Hashimoto, K.; Kobayashi, H.; Yoshida, S. *J. Chem. Soc., Faraday Trans.* **1990**, 86, 561.
- (16) Hill, T. L. *Introduction to Statistical Thermodynamics*; Addison-Wesley: Reading, 1962.
- (17) Ross, S.; Olivier, J. P. *On Physical Adsorption*; Interscience: New York, 1964.
- (18) *Handbook of Chemistry and Physics*, 56th ed.; Weast, R. C., Ed.; CRC Press: Cleveland, 1975.
- (19) Knox, J. H. *Molecular Thermodynamics*; Wiley: Chichester, 1978.
- (20) Atkins, P. W. *Physical Chemistry*, 5th ed.; Oxford Univ. Press: Oxford, 1995.
- (21) Thamm, H. *Zeolites* **1987**, 7, 341.