Methanol adsorption by amorphous silica alumina in the critical temperature range

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Abstract: The methanol adsorption capacity of an amorphous silica-alumina was measured using an equilibrium technique. The experimental temperature range was of 140 to 260 °C and the pure methanol pressure range was 0.1 to 1.2 MPa. A multilayer adsorption was found, also for temperatures above the critical temperature of the adsorbate. Based on the Jovanovic adsorption model, the mean residence times of the adsorbed molecules were calculated. Surprisingly, the heat of adsorption was found to be independent of the temperature in the multilayer adsorption range.

Key words: Methanol [67-56-1], high temperature adsorption, silica-alumina, multilayers, adsorption heat.

Notation

Symbols		Units
a	= parameter defined by Equation (7)	–
a'	= parameter defined by Equation (10)	Pa
$a(T)$	= parameter in the Peng-Robinson equation	$Pa/(mol/m^3)^2$
b	= parameter defined by Equation (8)	–
b'	= parameter defined by Equation (11)	Pa^{-1}
$b(T)$	= parameter in the Peng-Robinson equation	$m^3\ mol^{-1}$
c	= constant in the BET equation	–
k	= Boltzmann constant, being $1.3806 \cdot 10^{-23}$	$J K^{-1}$
K	= characteristic constant in the Peng-Robinson equation	–
m	= mass of one adsorbate molecule	kg
p	= pressure	Pa
q	= adsorption capacity	g/g
Q	= heat of adsorption	$J\ mol^{-1}$
R	= gas constant, being 8.314	$J\ mol^{-1}\ K^{-1}$
T	= absolute temperature	K
V	= molar volume	$m^3\ mol^{-1}$
x	= relative pressure ($= p/p_o$)	–
σ	= active molecule area	m^2
τ	= residence time	s
ω	= acentric factor	–

Introduction

A theoretical interpretation of the experimental equilibrium data for adsorption is still difficult, particularly at high absorbate pressures and temperatures. Generally, the reliability of the existent theoretical expressions for adsorption equilibria decreases rapidly with increasing pressure. In this paper, we present the results of our adsorption measurements for methanol on the low alumina, LAC-25 cracking catalyst of AKZO Amsterdam. We consider the multilayer adsorption theory of Jovanovic to be valid also above the critical temperature of the adsorbate. Therefore, we used his adsorption isotherm expressions to fit our experimental data.

Experimental

The experimental system is schematically shown in Figure 1. Prior to each experiment, the solid sample was dried for several hours at 280 °C under vacuum, weighted and placed in a $570 \cdot 10^{-6}$ m^3 autoclave. Subsequently, the air was evacuated from the autoclave at 280 °C and the apparatus was cooled to room temperature. A precisely measured volume of liquid methanol was then sucked into the autoclave. The valves V_1 and V_2 are used to evacuate the air and to inject the methanol samples, respectively. After evacuation and injection, plugs were installed on the valves in order to prevent leaking. The pressure in the autoclave was measured at several temperatures between 140 and 260 °C, each time after thermal stabilization of the system. An electronic pressure transducer was used for
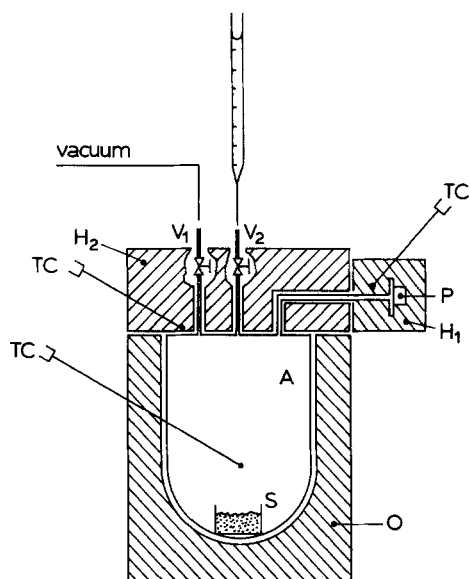
Fig. 1. The experimental set-up. Significance of symbols: $A = 570 \cdot 10^{-6}$ m^3 stainless steel autoclave; V_1 = valve for evacuation; V_2 = methanol injection valve; O = autoclave oven; H_1, H_2 = heating elements; TC = thermocouples; P electronic pressure transducer; S = sample

the pressure measurements. The temperature of the transducer was kept constant at 200 ± 0.1 °C, in order to prevent thermal drift of its calibration line. This procedure was repeated for various amounts of methanol injected, from 1 to $7 \cdot 10^{-6}$ m^3. The weight of the solid sample was 8.75 g. After the experiments, the composition of the gaseous autoclave contents was determined by means of gas chromatographic and NMR measurements. No decomposition products of methanol could be detected although dimethyl ether, for example, might be expected at the higher temperature levels investigated. There was no adsorption hysteresis observed, either. The same experimental procedure, but without the adsorbent, was used to obtain the most appropriate equation of state for methanol in the pressure and temperature range of our adsorption measurements.

Results

The amount of methanol adsorbed was calculated from the difference between the methanol pressure measured without and with the solid sample in the autoclave. Our experimental data obtained without the adsorbent were compared to the predictions of various equations of state for methanol. The experimental data agree well with the two-constant Peng-Robinson equation of state [1]:

$$ p = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)} \qquad (1) $$

in which

$$ a(T) = 0.45724 \frac{R^2 T_c^2}{P_c} (1 + K(1 - T_r))^2, \mathrm{N\,m^4 mol^{-2}} $$
$$ (2) $$

$$ K = 0.37464 + 1.54226\,\omega - 0.26992\,\omega^2 \qquad (3) $$

and

$$ b(T) = b(T_c) = 0.07780\,\frac{RT_c}{P_c}, \mathrm{m^3\,mol^{-1}} \qquad (4) $$

where ω is the acentric factor for methanol. In Figure 2 our experimental data are compared with the predictions of the Peng-Robinson and the Beattie-Bridgeman [2] equations of state. On the vertical axis the procentual differences in the predictions of pressure are plotted, with respect to the measured ones. Other equations of state, e. g. the virial equation, gave differences of more than 2 % with respect to our results. Equation (1) gives also a good fit of the p-V-T data for methanol found in Literature [2,3], and therefore we used it in the calculations.

Based on the most recent vapour-liquid equilibrium data for methanol by Ambrose et al. [4] we recalculated a value of 0.564 for the acentric factor of methanol, with the relation:

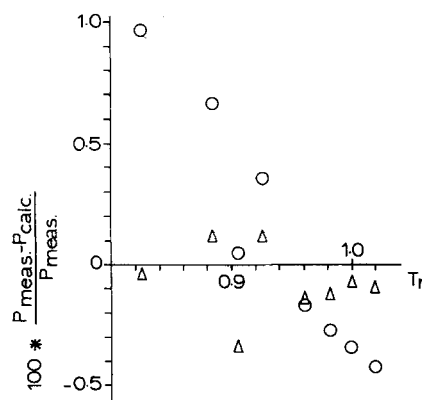$$ \omega = -\log_{10} (P_r^{\mathrm{sat}})_{T_r = 0.7} - 1. $$

Fig. 2. Comparison of the experimental p-V-T data with the predicted values with the Peng-Robinson ($\triangle$) and Beattie-Bridgeman ($\bigcirc$) equations of state. $5.5 \cdot 10^{-6}$ m^3 methanol injected into the $570 \cdot 10^{-6}$ m^3 autoclave

Table 1. Surface area distribution of the low alumina cracking cata-
lyst[a])

Pore diameter range nm	Surface area m²/gram
2.0– 3.0	92.6
3.0– 4.0	101
4.0– 5.0	138.1
5.0– 6.0	89.2
6.0– 7.0	38.4
7.0– 9.0	31
9.0–13.0	10

[a]) These results were obtained in a BET apparatus. It was
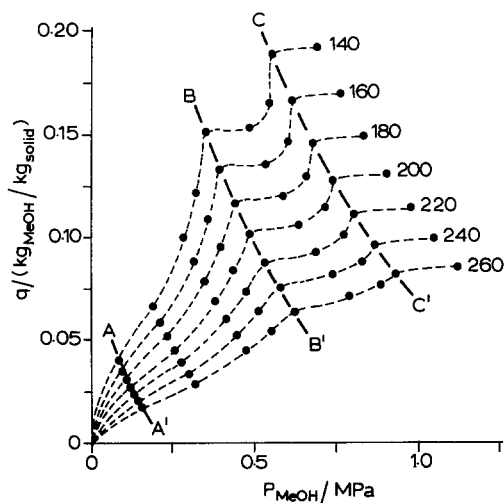assumed that all pores have a cylindrical shape.

Fig. 3. The adsorption isotherms for methanol on the silica-alumina
cracking catalyst. Parameter is the temperature in °C

The pore diameter distribution of the adsorbent was
determined using the usual BET technique; the results
are given in Table 1. The measured adsorption iso-
therms are shown in Figure 3.

Discussion and interpretation

It is obvious that the complicated profile of our iso-
therms cannot be described by any of the usual adsorp-
tion isotherm expressions, such as the BET isotherm
or its modifications, for example.

A surface area determination by the BET method
gave the value of 505 ± 9 m²/g solid. Taking the value
of 0.212 nm² for the effective area of one adsorbed
methanol molecule [5], the maximum possible mono-
layer capacity is 0.127 g MeOH/g solid, while our ex-
perimental results for the adsorption capacity go up to

0.192 ± 0.006 g/g. This indicates a multilayer adsorp-
tion. Another feature of our adsorption isotherms sup-
porting the multilayer adsorption hypothesis is the
convexity of the isotherms toward the pressure axis in
the range between the lines AA' and BB' in Figure 3
and the apparent existence of an inflexion point in the
left part of this area. Such S-shaped isotherms are com-
monly considered to correspond with multilayer
adsorption.

This inference is in disagreement with the essential
assumption of the multilayer adsorption theories as
given by Hüttig [6], Brunauer, Emmett and Teller [7]
and modifications of the BET theory [8–12]. Accord-
ing to these authors multilayer formation should be
impossible in our pressure and temperature range,
which is above the boiling point of methanol.

As is well known the BET equation given by Equa-
tion (5)

$$\frac{q}{q_m} = \frac{cx}{(1-x)(1-x+cx)} \qquad (5)$$

is quite inaccurate for relative pressures higher than 0.6
or 0.7. Usually $c \gg 1$ [7], further the term $(1 - x)$ in the
denominator of the BET expression becomes signifi-
cant at high pressures making the isotherm convex
towards the pressure axis. Although $(1 - x)$ gives a
correct "boundary" behaviour of the isotherms at
pressures tending to the saturation pressure of the
adsorbate, the quantitative description of the multi-
layer adsorption is still inaccurate if $\frac{1}{(1-x)}$ becomes
significant. Generally, the modifications of the BET
theory all introduce correction terms to the heat of
liquefaction for the subsequent adsorbed layers, still
using the saturation pressure as a temperature depend-
ent parameter. In this manner, the saturated vapor
pressure is being ascribed to a "liquid-like" adsorbed
phase consisting of a number of adsorbed layers having
different binding energies. This approach is rather
dubious in our opinion.

In 1969 Jovanovic [13] proposed a new adsorption
theory for a homogeneous surface without lateral in-
teractions between the adsorbed molecules. The Jova-
novic isotherm is expressed by the following equation:

$$q = q_m \{1 - \exp(-ax)\} \exp(bx) \qquad (6)$$

where q is the adsorbed amount, q_m is the monolayer
adsorption capacity, and x is the relative pressure,
defined as the ratio of the adsorbate pressure to its satu-

ration pressure. The term $1 - \exp(-ax)$ represents the monolayer adsorption, and the term $\exp(bx)$ is the correction for the multilayer adsorption. The parameters a and b describe the monolayer and multilayer adsorption, respectively:

$$a = \sigma \tau p_o / \sqrt{2\pi m kT} \qquad (7)$$

$$b = \sigma \tau_L p_o / \sqrt{2\pi m kT} \qquad (8)$$

where σ is the active area of one adsorbed molecule, p_o is the saturation pressure, and τ and τ_L are the mean residence times in the adsorbed state in the first and in the higher layers, respectively.

Jovanovic assumed for the case of a multilayer adsorption that the molecules adsorbed in the higher layers do not deprive the molecules in the underlying layers of their capability for desorption. The adsorbed phase is thus considered as a zone of compressed gas rather than a liquid-like phase. Therfore, the phenomenon of multilayer adsorption has no relation at all to the saturation pressure and Equations (6)–(8) have to be rewritten for *multilayer* adsorption as follows:

$$q = q_m \{1 - \exp(1 - a'p)\} \exp(b'p) \qquad (9)$$

with

$$a' = \sigma \tau / \sqrt{2\pi m kT} \qquad (10)$$

$$b' = \sigma \tau_L / \sqrt{2\pi m kT}. \qquad (11)$$

Equations (9)–(11) are essentially the original expressions obtained by Jovanovic. He used the relative pressure x in Equations (6)–(8), because, as he writes, in some cases it is more convenient to use relative instead of absolute pressures. In our opinion, the only advantage of Equations (6)–(8) is that they can be easily used for the elaboration of the literature data, as was done by Jovanovic in his subsequent paper [14]. A number of examples of the use of the Jovanovic equations in a dimensionless form can also be found in the Literature [15–17]. We believe that the equations of Jovanovic are also valid above the critical temperature of the adsorbate and therefore that the introduction of the saturation pressure is inappropriate.

If we only consider the lines to the left of the line $B - B'$ in Figure 3, our experimental isotherms can be treated as type II isotherms according to Jovanovic's classification. Jovanovic [13,14] and Yaronets and Yaronets [15] showed that the monolayer capacity q_m and the

multilayer adsorption parameter b can be obtained from the convex segment of the adsorption isotherm, because in a semi-logarithmic plot of q vs. x a straight line will be obtained with q_m as the intercept of the y-axis and with b as the slope. In our case the experimental points in the region between the lines AA' and BB' in Figure 3 form straight lines in the semi-logarithmic q vs. p plot as shown in Figure 4. The values of q_m and b' were calculated by linear regression; the results are presented in Table 2. It can be seen that the monolayer capacity q_m decreases with increasing temperature. Our experiments did not cover the low pressure range where the adsorption isotherms are expected to be concave toward the pressure axis. Therefore, we are not able to determine experimentally the monolayer adsorption parameter a'.
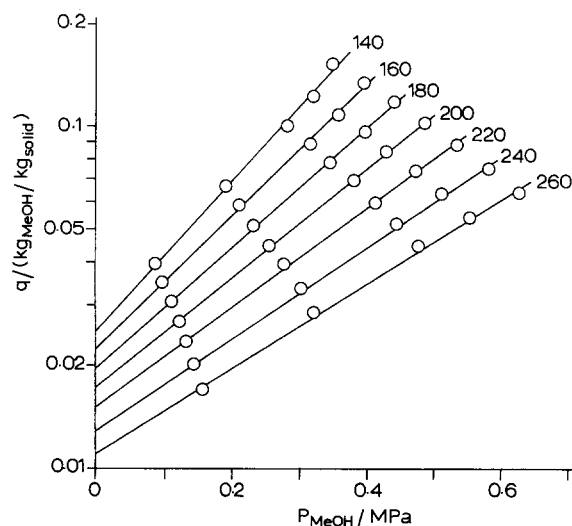

Fig. 4. The experimental adsorption capacity as a function of the methanol pressure. Parameter is the temperature of the system in °C

Table 2. The values of q_m and b'

T K	q_m g_{MeOH}/g_{solid}	$b' \cdot 10^6$ Pa^{-1}
413	0.0256	4.92
433	0.0226	4.39
453	0.0199	3.95
473	0.0175	3.59
493	0.0152	3.30
513	0.0131	3.07
533	0.0112	2.83

Table 3. The mean residence times of the adsorbed molecules

| T | $\tau_L \cdot 10^{10}$ |
K	s
413	5.06
433	4.63
453	4.26
473	3.96
493	3.72
513	3.52
533	3.32

As the active area of one adsorbed molecule σ is independent of the temperature [13] the mean residence times of the adsorbed molecules can be calculated using Equation (11). In compliance with the theory of Jovanovic we took a value of 0.424 nm² for σ, being the effective area of one admolecule multiplied by two. The calculated values of τ_L as a function of the temperature are shown in Table 3.
Based on Equation (12), the heat of adsorption can be calculated for the multilayer range [13,14,18]:

$$\tau_L = \tau_{(o)L} \exp\left(\frac{-Q_L}{RT}\right). \tag{12}$$

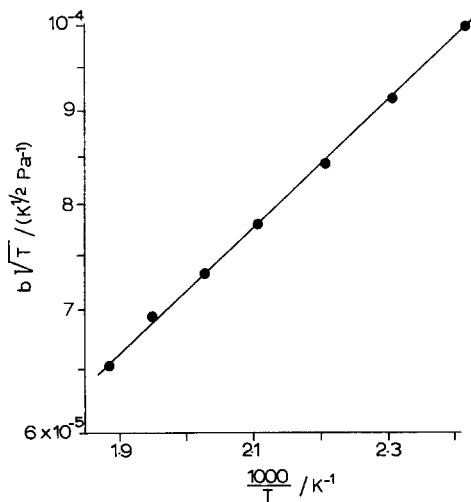Substituting Equation (12) into Equation (11) and plotting $b'\sqrt{T}$ vs. $1/T$ in a semi-logarithmic plot, the value of Q_L/R is obtained from the slope of the straight line, provided Q_L is independent of the temperature. The result is shown in Figure 5. It can be seen that Q_L is indeed independent of temperature. After linear regression we found a value of -6430 J/mol for Q_L. This is equal to the heat of condensation of methanol at 237.7 °C, just below the critical temperature [19]. Further, from the linear regression we derive a value of $7.76 \cdot 10^{-11}$ s for $\tau_{(o)L}$. This is a very large value when compared to the value of 10^{-13} s as suggested by de Boer [18] for this parameter.

A quantitative interpretation of our adsorption isotherms in the high methanol pressure range (on the right of the line BB' in Fig. 3) is much more difficult. Their stepwise form is analogous to the type IV and VIII isotherms in the classification of Jovanovic. However, he explains the occurrence of the irregular steps by capillary condensation phenomena. As already mentioned above, the pressure and temperature range of our experiments is far removed from the region of methanol condensation and capillary condensation is out of the question. In our opinion, the existence of the two "retortion points" on every isotherm — which agree with the points of intersection of the isotherms with the lines BB' and CC' in Figure 3 — is possibly related to the pore diameter distribution and surface area distribution of the adsorbent as given in Table 1.

A peculiarity can be observed in the shape of the isotherms in Figure 3: the ratio of the adsorption capacity at the "retortion point" to the calculated monolayer capacity is nearly equal for every isotherm. For the first "retortion points" — corresponding to the line BB' — this ratio approximately amounts to 5.5 to 5.9 while for the higher "retortion points" — line CC' — it lies between 7.3 and 7.6.

The decrease in the slope of the isotherms in the higher region is possibly caused by the fact that at sufficiently high adsorbate pressures the pores with diameters smaller than a certain value are completely filled with the adsorbate. For cylindrical pores, the number of adsorbed molecules in each succeeding layer will decrease, while for crevice pores it will remain constant. We do not know which pore shapes actually occur in our solids. Another difficulty is to ascribe a value to the thickness of one adsorbed layer. Moreover, we do not know whether the layer thickness will remain the same for each subsequent layer. Due to these unknown factors a quantitative description of the isotherms for the higher adsorbate pressures is impossible.

Fig. 5. The temperature dependence of $\sigma\tau_L/\sqrt{2\pi m k}$ in Equation (11)

Conclusions

The Peng-Robinson equation of state was found to give an accurate representation of the experimental data for methanol, at reduced pressures of up to 0.15 and in the reduced temperature range of 0.8 to 1.05. Based on the recent literature data a value of 0.564 was found for the acentric factor of methanol, as distinct from the value of 0.556 which is commonly reported in the literature.

From the experimental results obtained it can be concluded that multilayer adsorption is possible at temperature above the boiling point, even beyond the critical temperatures of the adsorbate. The Jovanovic multilayer adsorption model was found to be valid in this temperature range. The heat of multilayer adsorption calculated from his model was found to be temperature independent. We have not found any experimental adsorption data obtained at conditions comparable to those of our experiments in the literature, so we have no support from other experiments for this rather surprising result.

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