

Co-adsorption of 1,2-dichloroethane and 1-bromo,2-chloroethane on zeolite ZSM-5 from the liquid and vapour phases, using the Myers-Prausnitz-Dubinin model

Bénédicte Garrot ^a, Gaëtan Couderc ^b, Marie-Hélène Simonot-Grange ^a,
Fritz Stoeckli ^{b,*}

^a *Laboratoire de Recherche sur la Réactivité des Solides, Université de Bourgogne-CNRS UMR 5613, BP 47870, 21078 Dijon Cedex, France*

^b *Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, Case Postale 2, CH-2000 Neuchâtel, Suisse, Switzerland*

Abstract

The adsorption/co-adsorption of 1,2-dichloroethane (DCA) and 1-bromo,2-chloroethane (BCA) from the vapour and the liquid phases by zeolite ZSM-5 at ambient temperature is reported, using Dubinin's theory and the recent Myers-Prausnitz-Dubinin (MPD) theory. For adsorption from the liquid phase, the activity coefficients in the adsorbed and the liquid states are the same and no selectivity is observed. This is confirmed by the absence of an excess enthalpy of immersion of ZSM-5 into the mixtures. Adsorption from the vapour phase proceeds in two stages, as indicated by double Dubinin-Astakhov (DA) plots. If one considers only the domain of high relative pressure, co-adsorption is described by the MPD theory. The agreement between calculated and experimental compositions of adsorbate can be improved by using, as a first and good approximation, the activity coefficients of the liquid–solid equilibrium at the same composition. A good agreement is also observed between the enthalpies of immersion calculated from the DA equation and the experimental integral heats of adsorption. However, for vapour mixtures ZSM-5 shows selectivity in favour of the more volatile compound, 1-bromo,2-chloroethane. This probably results from adsorption at low pressures and could be due to differences in kinetics.

Keywords: Volatile organic compounds; Zeolite ZSM-5; Vapour–solid and liquid–solid adsorption; Kinetics; Immersion calorimetry; Dubinin's theory

1. Introduction

The aim of the present study was to investigate the binary co-adsorption of 1,2-dichloroethane

(DCA) and 1-bromo,2-chloroethane (BCA) at 298 K by zeolite ZSM-5, within the framework of the newly proposed Myers-Prausnitz-Dubinin (MPD) theory [1–3]. This approach combines the formalism developed by Myers and Prausnitz [4,5] for the description of binary and multiple co-adsorption, with the Dubinin-Astakhov (DA) equation [6–8]. The latter has the advantage that it describes

* Corresponding author. Fax: +41-32-718-25-11.
E-mail address: fritz.stoeckli@unine.ch (F. Stoeckli).

Nomenclature

DA	Dubinin-Astakhov equation	θ	filling coefficient defined as N^a/N_0^a
E	characteristic energy of adsorption	x_i^a, x_i^l	mole fractions of i in the adsorbed state and in the liquid mixtures
MPD	Myers-Prausnitz-Dubinin theory	p_i	partial pressure of vapour i
Ψ	specific function of Myers and Prausnitz	p_i^0	reference pressure of vapour i in the adsorbed mixture
α	thermal expansion coefficient of liquids	p_s, p_{si}	saturation pressure, saturation pressure of i
γ_i^a, γ_i^l	activity coefficient of i in the adsorbed state and liquid mixtures	V_{mi}	molar volume of i in the condensed state
$\gamma_{LS}^a(i)$	activity coefficient of i for the solid-liquid equilibrium	W_0	total micropore volume
N^a, N_0^a, N_i^a	adsorbed amount, maximum adsorbed amount, adsorbed amount of species i (reduced isotherm)	$\Delta_i H$	enthalpy of immersion
		$\Delta_{ads} H$	integral enthalpy of adsorption

adsorption of vapours by nanoporous solids such as activated carbons, clays and zeolites [6]. In view of the simplicity of the parameters required by Dubinin's theory, predictions can be made for the adsorption over a large range of pressure and temperature. It is also possible to relate the parameters of the adsorption isotherm to the enthalpy of immersion into the corresponding liquids [8]. Interesting results have been obtained in the case of microporous carbons, including the problem of non-ideality in the adsorbed state [3]. As shown in the present study, the MPD formalism can be transposed to zeolites.

2. Theory

Dubinin's theory for the volume filling of micropores (TVFM) is summarized by its fundamental relation, the so-called DA equation, based on the thermodynamic potential $A = RT \ln(p_s/p)$:

$$N^a = N_0^a \exp[-(A/E)^n] \quad (1)$$

N^a is the amount (usually in mmol g^{-1}) adsorbed at temperature T and relative pressure p/p_s , and N_0^a is the limiting amount filling the micropores. Formally, the total micropore volume is $W_0 = N_0^a V_m$, where V_m is the molar volume in the adsorbed state. In the case of zeolites, with relatively

small individual cavities, V_m is not necessarily the same as in the liquid state. The so-called characteristic energy E depends on the system under investigation and in the case of carbons, scaling factors called affinity coefficients can be introduced for the adsorbate, relative to benzene. In the case of zeolites, however, due to variations in the chemical nature of the solid, this approach is limited. It also appears that exponent n varies between 2 and 4–5, as opposed to the domain of 1.5–3 for nanoporous carbons. It has also been shown that E and n are temperature invariant and, therefore, Eq. (1) can be used to predict the adsorption of single vapours over a wide range of pressure and temperature.

As shown in detail elsewhere [8], a thermodynamic treatment of Eq. (1) based on the temperature invariance of parameters E and n , leads to the following relation for $\Delta_i H$, the enthalpy of immersion of the microporous solid into the corresponding liquid:

$$\Delta_i H \text{ (J g}^{-1}\text{)} = N_0^a E (1 + \alpha T) \Gamma (1 + 1/n) \quad (2)$$

In this expression, α represents the expansion coefficient in the adsorbed state (usually assumed to be equal to the value in the liquid state) and Γ is the tabulated 'gamma' function.

Following Myers and Prausnitz [4,5], the fundamental requirement for the co-adsorption equi-

librium of two or several vapours (A, B, i) with partial pressures p_i , is the equality of the integrals Ψ_i of the reduced individual isotherms:

$$\Psi_i = \int_0^{p_i^0} N_i^a(p)/p dp \quad (3)$$

In this expression, p_i^0 is an analogue of the saturation pressure of the pure liquid, p_{si} . Following Myers and Prausnitz, it is linked to the partial pressure of i at adsorption equilibrium, p_i , by an analogue of Raoult's law, so that $p_i = p_i^0 x_i^a \gamma_i^a$.

The quantities x_i^a and γ_i^a denote, respectively, the mole fraction of compound i and its activity coefficient in the adsorbed state. If one used the DA Eq. (1) as the individual isotherm $N_i^a(p)$, one obtains at equilibrium, with partial pressure p_i

$$\Psi_i(p_i) = (N_{0,i}^a E_i / RT) \times (1/n) \Gamma[1/n; (A_i \ln(p_{si} x_i^a \gamma_i^a / p_i))^n] \quad (4)$$

$N_{0,i}^a$ can also be replaced by the quantity W_0/V_{mi} , in agreement with the formalism used for microporous carbons. For binary adsorption, where $x_A^a + x_B^a = 1$, the equilibrium condition $\Psi_A = \Psi_B$ leads to x_A^a , if one postulates that the activity coefficients $\gamma_i^a = 1$ (hypothesis of an ideal adsorbed state (IAS) [5]). In the case of activated carbons, it has been shown that for micropore fillings $\theta = N^a/N_0^a$ above 0.3–0.4, the use of the activity coefficients $\gamma_{SL}^a(i)$ corresponding to the liquid–solid equilibrium (saturation: $\theta = 1$) leads to a very good overall agreement between the experimental and the calculated compositions x_i^a . This is also suggested by the fact that the standard deviation

$$\sigma = \sqrt{\Sigma[(\Psi_{DCA} - \Psi_{BCA})/\Psi_{DCA}]^2/n} \quad (5)$$

is typically around 0.08, when using all experimental parameters (p_i, x_i^a, γ_i^a) against values as high as 0.15 or more, if one assumes IAS [3]. The use of $\gamma_{SL}^a(i)$ reduces considerably the differences in the region of Henry's law. Consequently, there is no reason, why the assumption regarding the activity coefficients should not apply, at least to a first

approximation, to the case of binary co-adsorption by zeolites.

3. Materials and experimental techniques

Zeolite ZSM-5 (Wessalith DAZ; Si/Al > 500), obtained by direct synthesis, was supplied by *De-gussa AG* in the form of pellets containing approximately 20 wt.% of an inert clay binder.

Per unit cell, this zeolite contains a four connected framework composed of straight and sinusoidal channels, all accessible to the volatile organic compounds (VOC) used in the present study. The adsorbed amounts are expressed either in $\text{cm}^3 \text{g}^{-1}$ of solid without binder, or in molecules $(1/4 \text{ u.c.})^{-1}$ (molecules per 1/4 of unit cell, i.e. per unity of cavities that is one portion of straight channel, one portion of sinusoidal channel and one intersection).

Adsorption isotherms and heats of adsorption and co-adsorption were determined with the help of a specific experimental device consisting of a Calvet-type differential-flow calorimeter coupled with a volumetric line (manometry), using samples of 0.150 g, as described elsewhere [9,10]. The reversibility of the isotherms was verified by TGA under controlled vapour pressure (Mac-Bain spring balance using around 0.015 g). The measurements were carried out at 25 °C (298 K) on samples previously outgassed at 300 °C under 0.1 Pa (10^{-3} mbar) for 8 h (2% weight of adsorbed water was removed). The experimental uncertainty on the adsorbed amount was 2%, and 1% on the pressure. The relative error on the heats of adsorption was 5%.

Immersion calorimetry was carried out at 298 K on samples of 0.050–0.250 g, as described elsewhere [3,8], the samples being subjected to the same preparation as in the case of vapour adsorption. The experimental uncertainty on the enthalpies was around 2%. The activity coefficients in the adsorbed state at complete micropore filling, $\gamma_{SL}^a(i)$, were determined from the liquid–solid equilibrium by measuring the change in concentration of the liquid phase [3] and by using the mass balance of the two compounds. In the present case, the activity coefficients in the liquid

mixture, γ_i^1 , are calculated following the incremental technique proposed by Fredenslund et al. [11].

4. Results and discussion

4.1. Adsorption of the single compounds at 298 K

4.1.1. Adsorption from the vapour phase

The individual adsorption isotherms of DCA and BCA on zeolite ZSM-5, shown in Fig. 1, are of type I. It appears that BCA, the less volatile compound, is adsorbed more readily than DCA, before reaching the same saturation value of approximately 2.7 molecules $(1/4 \text{ u.c.})^{-1}$. Inspection of the low pressure region suggests an extended domain for Henry's law (Table 1).

More information is provided by the analysis in terms of Dubinin's theory. As illustrated by Fig. 2,

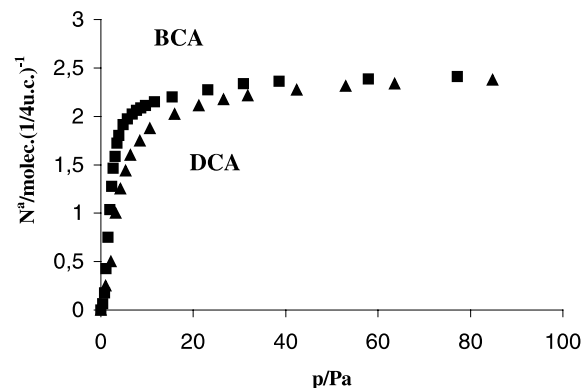


Fig. 1. Adsorption isotherms of DCA and BCA on zeolite ZSM-5 at 298 K.

Table 1

Henry's law for the adsorption of DCA and BCA by zeolite ZSM-5 at 25 °C

Compound	Domain	Inverse of Henry's constant ^a (molecules $(1/4 \text{ u.c.})^{-1} \text{ Pa}^{-1}$)
DCA	$\theta \leq 0.42$ or $N^a \leq 1.14$ molecules $(1/4 \text{ u.c.})^{-1}$	0.292
BCA	$\theta \leq 0.59$ or $N^a \leq 1.55$ molecules $(1/4 \text{ u.c.})^{-1}$	0.551

^a Slope of isotherm: $1/K_H = N^a/p$.

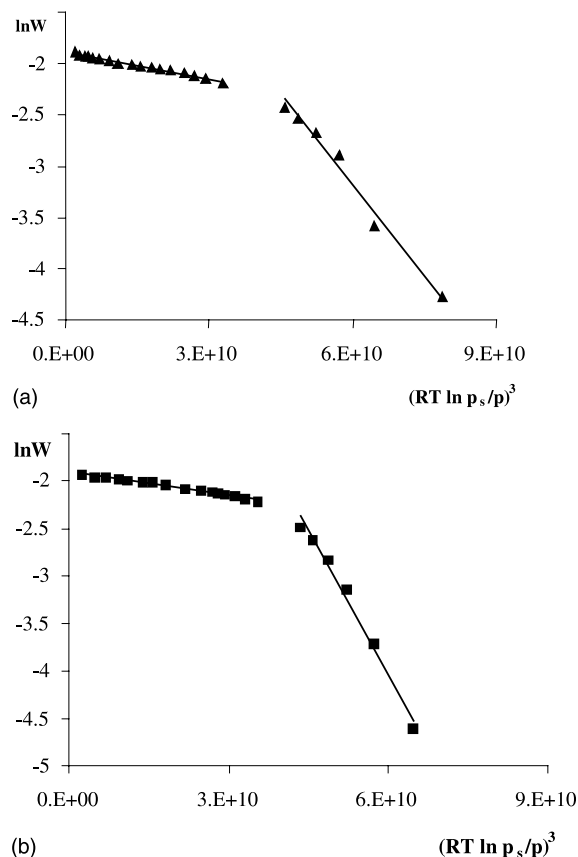


Fig. 2. Logarithmic plots of the DA Eq. (1) for the adsorption of DCA (a) and BCA (b) by zeolites ZSM-5 at 298 K. The best fits lead to $n = 3$ for both adsorbates.

the adsorption of DCA and BCA verifies two linear sections which correspond to Eq. (1) with exponent $n = 3$ in both cases. In the upper section of high pressures (micropore filling $\theta > 0.65$), the characteristic energies are of the same order of magnitude for both compounds (Table 2). This is not too surprising in view of the fact that the two adsorbates have very similar physical properties. On the other hand, for the initial section, at low relative pressures (micropore filling $\theta < 0.65$), one obtains lower values for the characteristic energies E (Table 2). Normally, the initial section should have a higher energy, and consequently a smaller slope than the upper section. This behaviour appears to be in contradiction with the results of immersion enthalpies and may be due to slow adsorption kinetics at low vapour pressures.

Table 2

Parameters of the DA Eq. (1) for the adsorption of DCA and BCA by zeolite ZSM-5 at 298 K with $n = 3.0$ for both adsorbates

Compound	Domain	E (kJ mol ⁻¹)	N_0^a (molecules (1/4 u.c.) ⁻¹)	W_0 (cm ³ g ⁻¹) ^a
DCA	$\theta > 0.64$ or $N^a > 1.75$ molecules (1/4 u.c.) ⁻¹	24.3	2.73	0.15
	$0.09 < \theta < 0.64$	13.6		
BCA	$\theta > 0.68$ or $N^a > 1.8$ molecules (1/4 u.c.) ⁻¹	25.5	2.65	0.15
	$0.03 < \theta < 0.68$	12.6		

^a W_0 calculated from the adsorbed species as in the liquid state.

4.1.2. Enthalpies of immersion: comparison with heats of adsorption

The experimental enthalpies of immersion of zeolite ZSM-5 into liquid DCA and BCA at 298 K are, respectively, (in absolute value, the process being exothermic): 54.7 ± 0.8 and 57.7 ± 1.2 J g⁻¹ (gram of zeolite), i.e. 64.4 ± 0.9 and 70.8 ± 1.5 kJ mol⁻¹ (mole of adsorbate). Calculations based on two contributions from Eq. (2), corresponding to both sections of the DA plots (Fig. 2), lead to enthalpies of immersion of 40.0 J g⁻¹ for both DCA and BCA, i.e. 56.3 kJ mol⁻¹ for DCA and 61.8 kJ mol⁻¹ for BCA. These values are much lower than found experimentally. However, if one considers only the section of high pressures extrapolated to low pressures, the calculated values are, respectively, 52.5 and 54.2 J g⁻¹, i.e. 62.9 and 69.5 kJ mol⁻¹, in good agreement with the experimental values. This suggests that in the case of liquids, the micropore filling corresponds to a process reflected by the upper section of the DA plot only.

The integral enthalpies of adsorption of the pure components from the vapour phase near saturation are calculated from the differential enthalpies [10,12]. The corresponding values, 54.6 ± 2.7 kJ mol⁻¹ for DCA and 58.8 ± 2.9 kJ mol⁻¹ for BCA (mole of adsorbate), or 36.5 and 35.3 J g⁻¹ (gram of solid), compared with those calculated from the enthalpies of immersion ($-\Delta_i H + \Delta_{\text{vap}} H$), show differences of 10.0 and 12.0 kJ mol⁻¹. However, they are of the same order of magnitude (slightly smaller and probably due to errors of integration at limits $\theta = 0$ and 1) as calculations based on two contributions from Eq. (2), corresponding to both sections of the DA plots.

These results suggest, that at low pressures the vapours do not see the entire micropore volume

because of a diffusional constraint, as opposed to the liquids, which penetrate into the zeolites under normal atmospheric pressure. Indeed, the study of the adsorption kinetics in the vapour the phase of these compounds, at 298 K and low pressures [10,12], showed particular behaviours, suited to a single-file diffusion process in one-dimensional channels when the guest molecules have dimensions close to those of the channels, as it is the case with many compounds adsorbed in materials with the MFI topology [13].

4.2. Co-adsorption of binary mixtures at 298 K

4.2.1. Solid-liquid equilibrium and enthalpies of immersion

The study of the solid-liquid equilibrium leads to the activity coefficients in the adsorbed state, γ_{SL}^a (BCA) and γ_{SL}^a (DCA), on the basis of the general relation

$$\gamma_{\text{SL}}^a(i) = \gamma_i^1 x_i^1 / x_i^a \quad (6)$$

Following Fredenslund et al. [11] and with the convention that $x_i = x_{\text{DCA}}$, the activity coefficients are given by

$$\begin{aligned} \gamma^1(\text{DCA}) = & -0.142x^3 + 0.5019x^2 - 0.6027x \\ & + 1.2421 \end{aligned} \quad (7)$$

$$\begin{aligned} \gamma^1(\text{BCA}) = & -0.0751x^3 + 0.3411x^2 - 0.0623x \\ & + 1.005 \end{aligned} \quad (8)$$

The fit of the experimental values of γ_{SL}^a , shown in Fig. 3, leads to

$$\begin{aligned} \gamma_{\text{SL}}^a(\text{DCA}) = & 0.0663x^3 + 0.0341x^2 - 0.2671x \\ & + 1.1668 \end{aligned} \quad (9)$$

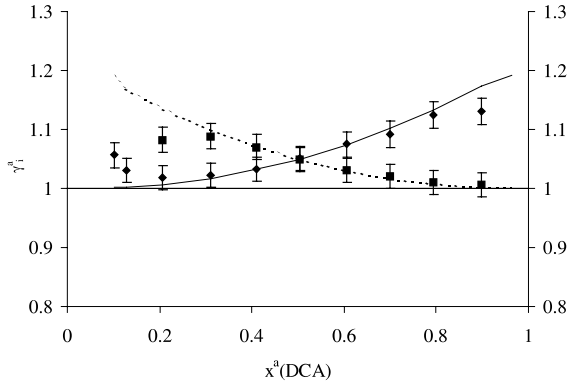


Fig. 3. Activity coefficients of DCA and BCA in the liquid mixtures (curves) and in the adsorbed state (BCA ◆) (DCA ■), at 298 K.

$$\gamma_{\text{SL}}^{\text{a}}(\text{BCA}) = 0.1274x^3 + 0.2871x^2 - 0.0048x + 1.0004. \quad (10)$$

(Note that slightly different expressions are used in the case of thermodynamic treatments involving activity coefficients, as suggested by Guggenheim [14]).

As shown in Fig. 3, in the domain $0.2 < x_{\text{DCA}} < 0.8$ and within experimental uncertainty, the activity coefficients of DCA and BCA are practically the same in the adsorbed phase at complete micropore filling and in the liquid phase, in agreement with the fact that $x_i^{\text{a}} = x_i^{\text{l}}$. It is interesting to point out that this behaviour contrasts with the case of DCA + C₆H₆ mixtures filling the micropores of a typical active carbon at 293 K [3,15]: whereas the liquid mixture is ideal ($\gamma^{\text{l}} = 1$) over the entire range of composition, it appears that $\gamma_{\text{SL}}^{\text{a}}(\text{DCA})$ and $\gamma_{\text{SL}}^{\text{a}}(\text{C}_6\text{H}_6)$ are different from unity. This shows the influence of the adsorbent on the mixture and, in the present case, it suggests that zeolite ZSM-5 does not modify the non-ideality of the DCA + BCA mixture at 298 K.

Following the arguments developed earlier [3], the fact that $\gamma_{\text{SL}}^{\text{a}}(i) = \gamma_i^{\text{l}}$ implies that there should be no excess enthalpy of immersion of ZSM-5 into mixtures of DCA + BCA. For a given composition x^{a} this quantity represents the difference between the experimental enthalpy of immersion and

the linear combination of the enthalpies of immersion into the pure liquids:

$$h_i^{\text{c}}(T; x^{\text{a}}) \text{ J/g} = \Delta_i H_{\text{exp}} - (N_{\text{DCA}}^{\text{a}} V_{\text{mDCA}}/W_0) \Delta_i H_{\text{DCA}} - (N_{\text{BCA}}^{\text{a}} V_{\text{mBCA}}/W_0) \Delta_i H_{\text{BCA}}. \quad (11)$$

In this expression, $N_{\text{DCA}}^{\text{a}}$ and $N_{\text{BCA}}^{\text{a}}$ represent the amounts of DCA and BCA adsorbed in the micropores at composition x^{a} . (A small correction due to the wetting of the external surface area can be omitted in the case of zeolites).

It appears, within experimental uncertainty, that $h_i^{\text{c}}(T; x^{\text{a}}) = 0$ over the entire composition range. (In the case of the microporous carbon and DCA + C₆H₆ mixtures, on the other hand, a relatively important excess enthalpy was observed, due to the non-ideality of the adsorbed phase). Immersion calorimetry provides therefore an independent test for self-consistency for the determination of the activity coefficients in the adsorbed state, $\gamma_{\text{SL}}^{\text{a}}$.

4.2.2. Solid–vapour equilibrium

Mixtures of DCA + BCA vapours were adsorbed at three initial compositions of the adsorptive (DCA: 18%, 55%, 67%). In the range of total equilibrium pressures p between 100 and 800 Pa, i.e. in a domain of filling coefficients larger than 0.65, the selectivity diagram $x_{\text{DCA}}^{\text{a}} = f(y_{\text{DCA}})$ shown in Fig. 4 (y_i : mole fraction in the vapour phase) indicates that the selectivity is always in favour of BCA, the more volatile compound. This selectivity is verified by the breakthrough curves [10,12]. For a total equilibrium pressure $p = 400$ Pa corresponding to a micropore filling θ close to 1, the selectivity, classically defined by the ratio:

$$\eta_{\text{DCA/BCA}} = \frac{x_{\text{DCA}}^{\text{a}} y_{\text{BCA}}}{x_{\text{BCA}}^{\text{a}} y_{\text{DCA}}} \quad (12)$$

is around 0.8. This result differs from the case of the liquid–solid system, where it is equal to unity (for any composition, same activity coefficients in both phases).

The integral enthalpies of co-adsorption from the vapour phase as a function of the composition close to the saturation are calculated from the differential enthalpies. Their values show a similar variation with composition as those calculated

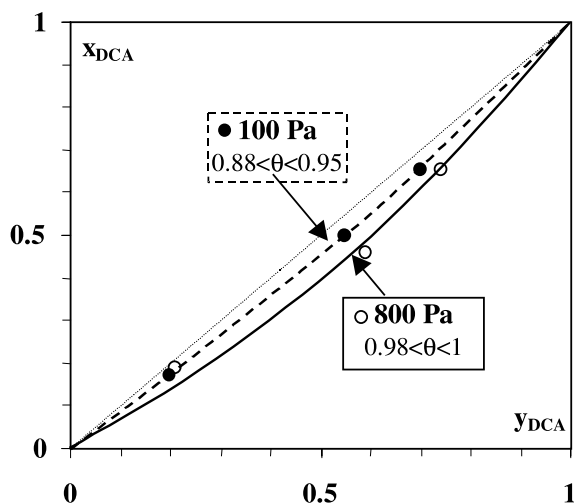


Fig. 4. Diagram of selectivity of DCA + BCA mixture at 298 K.

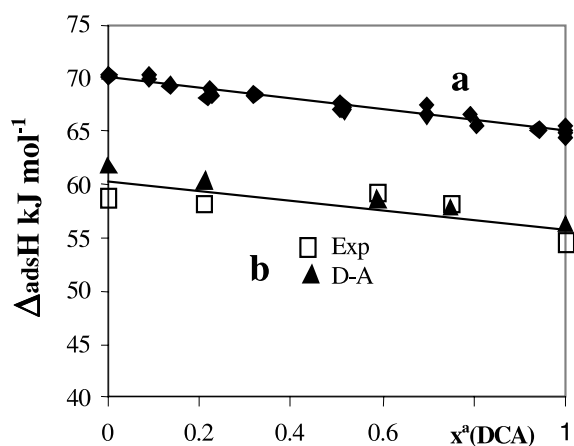


Fig. 5. Integral heats of adsorption for (a) the liquid–solid equilibrium (b) the vapour–solid equilibrium at 298 K, as functions of the average composition x_{DCA} .

from the enthalpies of immersion. However, like the pure compounds, they are lower and similar to those calculated from the DA plots (Fig. 5).

By analogy with the case of microporous carbons [3], the experimental data for co-adsorption of DCA and BCA from the vapour phase can be used to validate the MPD theory. This is done by examining the residual (Eq. 5) for a total of n different experiments. The hypothesis of an IAS,

where $\gamma^a = 1$, leads to $\sigma = 0.05$. On the other hand, if one uses the solid–liquid activity coefficients, $\sigma = 0.03$ (the fit cannot be improved, due to the experimental uncertainty). This indicates that γ_{SL}^a (DCA) and γ_{SL}^a (BCA) can be used as a first and good approximation for the activity coefficients γ_{SG}^a (DCA) and γ_{SG}^a (BCA) when their vapour mixtures are adsorbed at $\theta > 0.65$. This corresponds to the domain where adsorption from the vapour phase and the liquid phase (immersion) are in agreement.

In agreement with the results reported for other systems [3], it appears that for a given composition x^a the activity coefficients in the adsorbed state $\gamma^a(x^a)$ can be approximated by the coefficients $\gamma_{SL}^a(x^a)$. This approximation should be valid at least for degrees of micropore filling $\theta \geq 0.4$. It follows that the predictions based on MPD can also be greatly improved in the case of zeolites, but the problem of the ‘a priori’ determination of the activity coefficients γ_{SL}^a still remains. However, from the recent work of Berti et al. on selected zeolites, [16] it appears that predictions should be possible. By analogy with the work of Fredenslund et al. [11] on liquid mixtures, the former used a technique based on increments taking into account the chemical composition of the adsorbate and the adsorbent. Although limited to a few cases, this approach seems promising and its combination with MPD would provide a useful tool for the prediction of binary adsorption in microporous solids.

However, for adsorption from the vapour phase, ZSM-5 presents selectivity in favour of BCA. One may postulate that this selectivity results from the adsorption process at low pressures and corresponding to the first step in the DA plot. It probably reflects structural kinetics, which do not affect the liquids penetrating into the pores under atmospheric pressure.

5. Conclusions

The present study shows that the co-adsorption of mixtures of 1,2-dichloroethane + 1-bromo,2-chloroethane by zeolite ZSM-5 at ambient temperature is different in the liquid and the vapour

phases. In the liquid phase, ZSM-5 shows no selectivity, as opposed to the vapour phase where it favours the adsorption of the more volatile compound, 1-bromo,2-chloroethane. This is probably due to differences in adsorption kinetics at low pressures, conditioned by the structure of the zeolite.

Dubinín's theory, combined with enthalpies of immersion, is a very good approach for the study of the adsorption process in zeolites. One obtains a good agreement between the experimental and the calculated enthalpies of immersion of ZSM-5 into the pure liquids. In the case of the vapour mixtures adsorbed at $\theta > 0.65$, the use of the activity coefficients derived from the solid-liquid equilibrium improves the predictions of the MPD approach. However, it is not possible to predict the experimental selectivity, probably due to a specific kinetic behaviour at low pressures.

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