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The Myers–Prausnitz–Dubinin Theory and Non-ideal Adsorption in Microporous Solids

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ABSTRACT: The adsorption of vapour and liquid mixtures of benzene + 1,2-dichloroethane, chlorobenzene + carbon tetrachloride, chlorobenzene + cyclohexane and 1-bromo,2-chloroethane + 1,2-dichloroethane on two activated carbons and on two zeolites (UC13X and ZSM-5) was examined near room temperature. It was shown that the combination of the recent Myers–Prausnitz–Dubinin (MPD) theory with the activity coefficients of the corresponding solid–liquid equilibrium leads to a good correlation between the calculated and the experimental mole fractions for binary vapour adsorption by microporous solids. This confirms that the approach based on an ideal adsorbed state (IAS) can be improved by using these activity coefficients as a first and good approximation.

INTRODUCTION

As shown by Lavanchy *et al.* (1996), the binary adsorption of vapours by microporous solids can be described by a combination of the theories of Myers and Prausnitz (Myers and Prausnitz 1965; Valenzuela and Myers 1989) and of Dubinin (Dubinin 1989; Stoeckli 1993, 1995). The new approach, called MPD theory, provides a useful basis for the calculation of such adsorption under static (Stoeckli *et al.* 1997, 2000) and dynamic conditions (Lavanchy and Stoeckli 1997, 1999).

In the case of binary adsorption, straightforward calculations lead to the prediction of the composition x^a, if one assumes an ideal adsorbed state (IAS). However, as pointed out by Stoeckli *et al.* (1997, 2000), the predictive power of MPD is still limited by the non-ideality of the adsorbed phase. This means that relatively important deviations may be observed in the region of Henry's law and sometimes beyond. At the present time, no 'a priori' prediction can be made for the activity coefficient γ_i^a of species i in the adsorbed state, with the exception of certain systems involving specific zeolites (Berti *et al.* 1999). However, the adsorption of benzene + 1,2-dichloroethane mixtures by a typical active carbon at 293 K, from the vapour and the liquid phases (Stoeckli *et al.* 1997, 2000), suggests that the activity coefficients in the adsorbed state, $\gamma_i^a = \gamma_i^a (T;x_i^a)$ are very close to those measured for the solid–liquid equilibrium, γ^a_{LSi}. This corresponds to the complete filling of the micropores ($\theta = 1$) and a composition x^a in the adsorbed state. The use of these coefficients leads to a very good agreement between the calculated and the experimental mole fractions x_i^a of benzene and 1,2-dichloroethane in the range $0.05 < x_i^a < 1$ and for degrees of micropore filling $\theta > 0.3$.

This hypothesis appeared reasonable and, as reported here, was tested successfully for several mixtures adsorbed by activated carbons and by zeolites. This may be a first step in the improvement of the prediction of binary adsorption by microporous solids on the basis of MPD and other approaches.

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THEORY

As described in detail elsewhere (Lavanchy *et al.* 1996; Stoeckli *et al.* 1997, 2000), MPD combines Dubinin's equation (Dubinin 1988; Stoeckli 1995) with the formalism of Myers and Prausnitz (1965), which means that predictions can be made over a wide range of pressure and temperature, at least if one assumes an ideal adsorbed state. For the adsorption of a binary mixture of vapours A and B, the equilibrium condition is

$$\psi_A(T; p_A; x_A^a; \gamma_A^a) = \psi_B(T; p_B; x_B^a; \gamma_B^a) \qquad (1)$$

where p_A and p_B are the equilibrium pressures of vapours A and B, x_A^a and x_B^a are the equilibrium concentrations in the adsorbed state, with the corresponding activity coefficients γ^a. If the individual vapours follow the Dubinin–Radushkevich equation, the functions ψ are respectively:

$$\psi_A = (W_{oA}/V_{mA})(\beta_A E_{oA}/RT)(\pi^{1/2}/2)[1 + \mathrm{erf}\{(RT/\beta_A E_{oA}) \ln(p_A/p_{sA}\gamma_A^a x_A^a)\}] \qquad (2)$$

and

$$\psi_B = (W_{oB}/V_{mB})(\beta_B E_{oB}/RT)(\pi^{1/2}/2)[1 + \mathrm{erf}\{(RT/\beta_B E_{oB}) \ln(p_B/p_{sB}\gamma_B^a x_B^a)\}] \qquad (3)$$

W_{oA} and W_{oB} are the micropore volumes accessible to species A and B; V_{mA} and V_{mB} are the molar volumes of the liquids; β_A and β_B are their affinity coefficients with respect to benzene; E_{oA} and E_{oB} represent the characteristic energies for the individual isotherms. Pressures p_{sA} and p_{sB} are the saturation pressures of A and B at temperature T.

In the case of zeolites, where adsorption is often described by the more general expression of Dubinin and Astakhov (DA), the functions ψ_i are given by

$$\psi_i = (W_{oi}/V_{mi})(\beta_i E_{oi}/RT)(1/n)\, \Gamma[1/n; (RT/\beta_i E_{oi}) \ln(p_i/p_{si}\gamma_i^a x_i^a)\}] \qquad (4)$$

where Γ is the incomplete Gamma function (Gradshteyn and Ryzhik 1980) and n is the exponent of the DA equation. When n = 2, one obtains the Dubinin–Radushkevich equation, which leads to equations (2) and (3).

If one assumes an ideal adsorbed state ($\gamma_i^a = 1$), the compositions x_A^a and $x_B^a = 1 - x_A^a$ can be calculated from equation (1) with the help of the structural characteristics of the adsorbent (E_{oi}, W_{oi}, n), the molecular parameters of the vapours (V_{mi}, β_i, p_{si}) and the partial pressures p_i at equilibrium, which can be obtained from a mass balance. However, as pointed out above, for real systems deviations can be observed in the Henry's law domain, owing to the non-ideality of the corresponding adsorbate.

By analogy with the liquid state (Guggenheim 1967), activity coefficients in the adsorbed state can be described to a good approximation by general expressions of the type:

$$\gamma_A = \exp[(1 - x_A)^2(a_1 + a_2 x_A)/RT] \qquad (5)$$

and

$$\gamma_B = \exp[x_A^2(a_3 + a_4(1 - x_A))/RT] \qquad (6)$$

If necessary, the polynomials can be expanded to account for more complicated behaviours. This type of equation is convenient to obtain excess functions, as reported for the system benzene + 1,2-dichloroethane (DCA) adsorbed by an activated carbon at 293 K (Stoeckli *et al.* 2000).

The validity of the MPD theory can be tested by analyzing the residual

$$\sigma = \sqrt{\Sigma[(\psi_A - \psi_B)/\psi_A)]^2/n} \tag{7}$$

between the function ψ of components A and B, by using all the experimental data available for the n equilibrium points. As found earlier for the system C_6H_6 + DCA adsorbed on carbon U-02 (Stoeckli *et al.* 2000), and confirmed in the present study for a variety of systems, the use of the activity coefficients $\gamma^a_{i,s}$ as first approximations for the activity coefficients in the adsorbed state reduces σ considerably with respect to the hypothesis of an ideal adsorbed state. This may be regarded as a further and more refined test for the validity of MPD.

EXPERIMENTAL

Besides the system benzene + 1,2-dichloroethane adsorbed on carbon U-02 at 293 K already reported in detail (Blackburn *et al.* 1957; Stoeckli *et al.* 2000), we examined the adsorption of the following vapour and liquid mixtures:

(1) Benzene + 1,2-dichloroethane (DCA) on carbon U-02 and on zeolite UC13X(Na) at 293 K.
(2) 1-Bromo,2-chloroethane (BCA) + 1,2-dichloroethane (DCA) on zeolite ZSM-5 at 298 K, in collaboration with Garrot (2001).
(3) Chlorobenzene (CB) + carbon tetrachloride on carbon U-02 at 298 K.
(4) Chlorobenzene + cyclohexane on carbon U-03 at 293 K.

The choice of the system benzene + 1,2-dichloroethane was based on the fact that it is ideal in the liquid state (Coulson *et al.* 1948). It was also interesting to compare the adsorption of this mixture on two different microporous solids, activated carbon and zeolite UC13X(Na).

Adsorption from the vapour phase was investigated by using the so-called GC-Headspace technique (Lavanchy *et al.* 1996), but in the case of the system chlorobenzene + cyclohexane on carbon U-03 at 293 K the gas phase was also analyzed with the help of a quadrupole mass spectrometer (Balzers Ltd., type ThermoStar 300T3) in order to cross-check the data obtained with gas chromatography (GC). The agreement was excellent.

The activity coefficients $\gamma^a_{i,s}$ in the adsorbed phase in equilibrium with the liquid mixture (compositions x^a_i and x^ℓ_i) were determined as described previously (Stoeckli *et al.* 1997, 2000) and

$$\gamma^a_{i,s}(x^a_i) = \gamma^\ell_i(x^\ell_i) \cdot x^\ell_i / x^a_i \tag{8}$$

In the case of the pure liquid mixtures, the activity coefficients were either found in the literature or calculated on the basis of the UNIFAC model proposed by Fredenslund *et al.* (1977).

For the mixed adsorption of 1-bromo,2-chloroethane + 1,2-dichloroethane vapours on zeolite ZSM-5 at 298 K, the data was obtained as described by Garrot (2001). Enthalpies of immersion of the solids into liquid mixtures were also determined in order to cross-check the predictions for the adsorbed state, as suggested by the activity coefficients. This approach has been discussed in detail for the system benzene + 1,2-dichloroethane (Stoeckli *et al.* 2000).

The main characteristics of the solids and the adsorptives are given in Tables 1 and 2. In view of

TABLE 1. Micropore Volumes W_0 of the Solids Studied and Characteristic Energies E_i for the Various Adsorptives, as Obtained from the Dubinin–Astakhov Equation with Exponent n = 2 (Carbons) or 3 (Zeolites)

	Solid							
	U-02		U-03		UC13X(Na)		ZSM-5	
Adsorptive (i)	$10^{-3} W_0$ (m^3/kg)	E_i (kJ/mol)	$10^{-3} W_0$ (m^3/kg)	E_i (kJ/mol)	$10^{-3} W_0$ (m^3/kg)	E_i (kJ/mol)	$10^{-3} W_0$ (m^3/kg)	E_i (kJ/mol)
Benzene	0.448	17.0 (n = 2)	–	–	0.245	29.2 (n = 3)	–	–
1,2-Dichloroethane (DCA)	0.448	14.2 (n = 2)	–	–	0.234	43.64 (n = 3)	0.151	23.2 (n = 3)
1-Bromo,2-chloroethane (BCA)	–	–	–	–	–	–	0.151	25.5 (n = 3)
Cyclohexane	–	–	0.540	16.4 (n = 2)	–	–	–	–
Chlorobenzene (CB)	0.468	18.4 (n = 2)	0.560	17.2 (n = 2)	–	–	–	–
Carbon tetrachloride	0.467	17.5 (n = 2)	–	–	–	–	–	–

TABLE 2. Properties of Adsorptives Studied

	Adsorptive					
	C_6H_6	DCA	BCA	C_6H_{12}	CB	CCl_4
Molar volume, V_m (m^3/mol)						
293 K	88.97	78.92	–	108.1	101.7	96.5
298 K	89.41	79.45	82.46	–	102.22	97.09
Saturated pressure, p_s (Pa)						
293 K	9985	8339	–	9124	1250	12566
298 K	12689	10500	3911	–	1596	15250

the differences between microporous carbons and zeolites and between zeolites themselves, the affinity coefficients β lose their meaning and Table 1 therefore gives the values of the individual characteristic energies $E = \beta E_0$ obtained from the adsorption isotherms and to be used as such in equations (2)–(4).

RESULTS AND DISCUSSION

The activity coefficients of the different adsorptives in the liquid mixtures and the adsorbed phase in equilibrium with them, γ^ℓ and γ^a_{LS}, have been fitted to equations (5) and (6). The different systems provided the following results.

(1) Benzene + 1,2-dichloroethane (DCA) at 293–298 K

The liquid mixture is ideal, but in the case of adsorption on carbon U-02 (293 K) the corresponding activity coefficients

$$\gamma^a_{\mathrm{SL(DCA/U\text{-}02)}} = \exp[(1-x)^2(-1299 + 5033x)/RT] \tag{9}$$

$$\gamma^a_{\mathrm{SL(C_6H_6/U\text{-}02)}} = \exp[(1-x)^2(-3490 + -4707x)/RT] \tag{10}$$

where $x = x^a_{DCA}$, are relatively important. There was a small preferential adsorption of DCA at all concentrations.

Using these coefficients as first and good approximations for adsorption from the vapour phase leads to a significant reduction of the residual σ given by equation (7) from 0.13 (IAS) to 0.08. This is also reflected by the agreement between the calculated and experimental values of x^a, as shown in Figure 1.

For adsorption by zeolites UC13X(Na), one obtains

$$\gamma^a_{\mathrm{SL(DCA/UC13X)}} = \exp[(1-x)^2(943 + 59680x)/RT] \tag{11}$$

$$\gamma^a_{\mathrm{SL(C_6H_6/UC13X)}} = \exp[x^2(-6371 + 6272(1-x))/RT] \tag{12}$$

with $x = x^a_{DCA}$. The adsorbed phase is non-ideal and the use of the activity coefficients reduces the residual σ from 0.17 to 0.04.

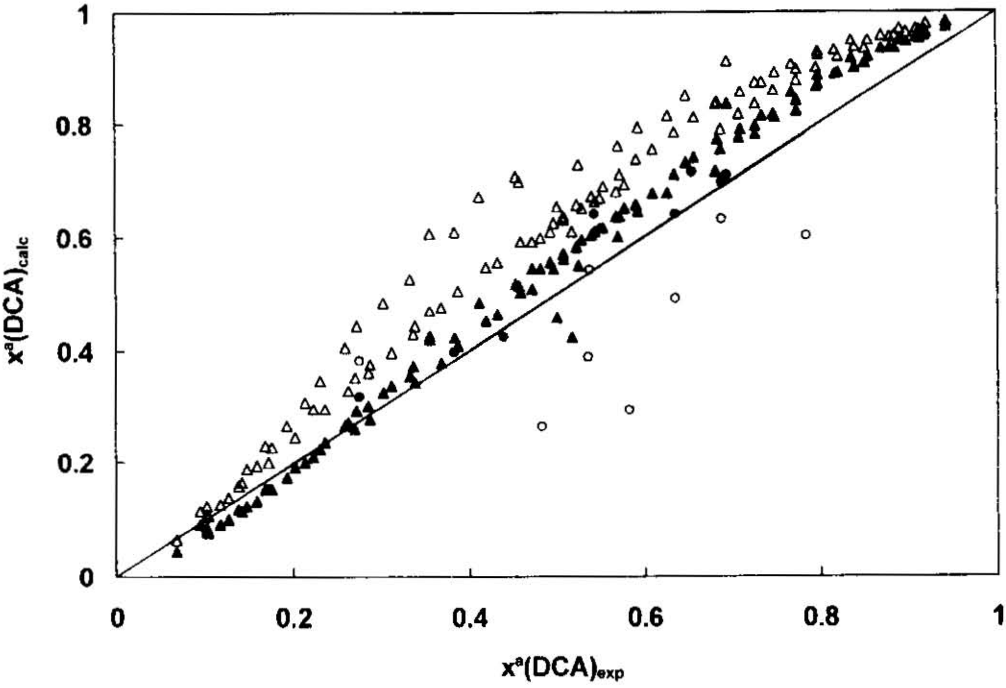

Figure 1. Correlation between the calculated and experimental mole fractions of binary mixtures of benzene + 1,2-dichloroethane (DCA) adsorbed on carbon U-02 at 293 K (Δ ▲) and zeolite UC13X(Na) at 293 K (○ ●); $x^a(C_6H_6)_{calc}$ obtained from equations (1)–(3) assuming an ideal adsorbed state (Δ ○) or using the activity coefficients $\gamma^a_{i,s}$ (▲ ●).

(2) 1-Bromo,2-chloroethane (BCA) + 1,2-dichloroethane (DCA) at 298 K

The liquid mixture is slightly non-ideal and in the case of zeolites ZSM-5 at 298 K it appears that within experimental uncertainty, $x^a = x^\ell$. This means that the activity coefficients

$$\gamma^a_{SL(BCA/ZSM-5)} = \exp[(1-x)^2(357+324x)/RT] \tag{13}$$

$$\gamma^a_{SL(DCA/ZSM-5)} = \exp[x^2(382+204(1-x))/RT] \tag{14}$$

($x = x^a_{BCA}$) are the same as those of the liquid mixture at the same composition. There is, nevertheless, a slight preference for the adsorption BCA from the vapour phase, which indicates that γ^a_{BCA} and $\gamma^a_{SL(BCA)}$ are slightly different. However, the use of γ^a_{SL} for the adsorption of the vapour mixtures reduces the residual σ from 0.05 to 0.03, since the non-ideality is not very strong in any case. As shown in Figure 2, one obtains very good agreement between the experimental and calculated values of x^a_{DCA} and consequently of $x^a_{BCA} = 1 - x^a_{DCA}$.

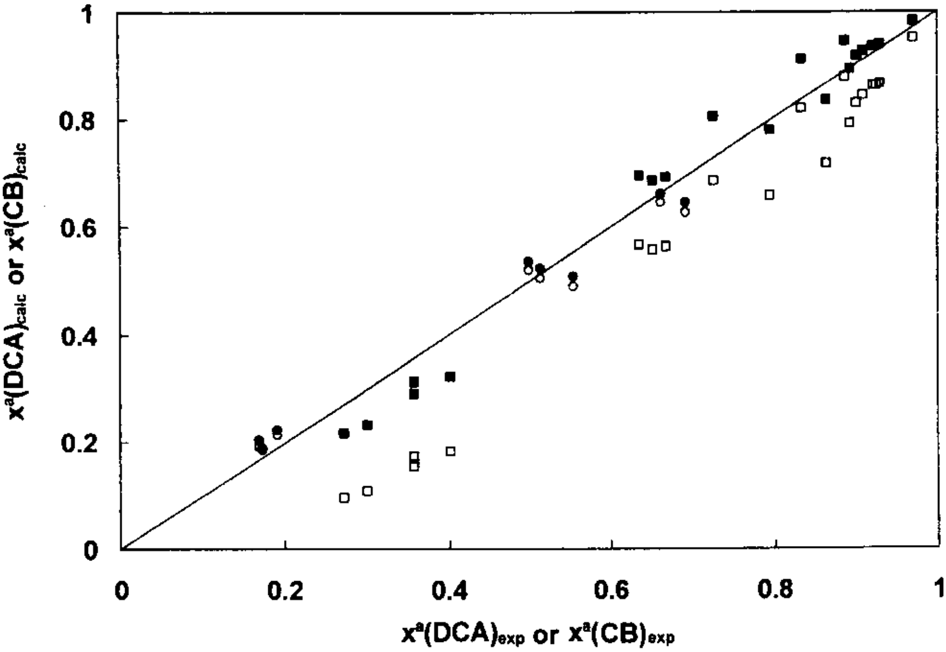

Figure 2. Correlation between the calculated and experimental mole fractions of binary mixtures of 1-bromo,2-chloroethane + 1,2-dichloroethane (DCA) adsorbed on zeolite ZSM-5 at 298 K (○ ●) and of chlorobenzene + carbon tetrachloride on carbon U-02 at 298 K (□ ■); $x^a(DCA)_{calc}$ and $x^a(CCl_4)_{calc}$ obtained from equations (1)–(3) assuming an ideal adsorbed state (○□) or using the activity coefficients γ^a_{LS} (●■).

(3) Chlorobenzene (CB) + carbon tetrachloride (CCl_4) on carbon U-02 at 298 K

In this case, the activity coefficients may be written as

$$\gamma^{a}_{SL(CB/U\text{-}02)} = \exp[(1-x)^2(-3828+209x)/RT] \tag{15}$$

$$\gamma^{a}_{SL(CCl_4/U\text{-}02)} = \exp[x^2(2490-1389(1-x))/RT] \tag{16}$$

with $x = x^{a}_{CB}$. The liquid mixture and the adsorbed state (Lavanchy *et al.* 1996) are non-ideal and the use of γ^{a}_{SL} reduces the residual σ from 0.13 to 0.05. Figure 2 shows the agreement between the calculated and experimental values of x^{a}_{CB}.

(4) Chlorobenzene (CB) + cyclohexane on carbon U-03 at 293 K

Here, the activity coefficients are

$$\gamma^{a}_{SL(CB/U\text{-}02)} = \exp[(1-x)^2(4228-136.252x)/RT] \tag{17}$$

$$\gamma^{a}_{SL(C_6H_{12}/U\text{-}02)} = \exp[x^2(-2295-14513(1-x))/RT] \tag{18}$$

with $x = x^{a}_{CB}$. The liquid and the adsorbed state are both non-ideal and the use of γ^{a}_{SL} reduces the residual σ from 0.29 to 0.05. As shown in Figure 3, this also improves considerably the fit between the calculated and experimental values of $x^{a}_{C_6H_{12}}$.

From the study of these systems, it appears that in all cases the use of the activity coefficients γ^{a}_{SL} as a first approximation for the actual coefficients γ^{a} for adsorption from the vapour phase reduces the residual σ to approximately 0.05 (this is comparable with the experimental uncertainties on γ^{a}_{SL} and on x^{a}). As illustrated by Figures 1–3, the use of γ^{a}_{SL} in the fundamental equation (1) also improves the agreement between the calculated and experimental values of x^{a}, the quantity to be determined by MPD. The improvement is obvious in the region of Henry's law where deviations from ideality may be considerable for the corresponding adsorptives. This agreement, observed for five different systems, may be regarded as a further test for the MPD approach.

From the foregoing, we may conclude that MPD can be used with a variety of systems and the quality of its predictions for the adsorption of binary vapour mixtures is much improved if one uses the activity coefficients γ^{a}_{SL} to a first and good approximation. The latter correspond to complete filling of the micropores ($\theta = 1$), but it appears that in the case of adsorption from the vapour phase with $\theta > 0.3$, γ^{a}_{SL} is a good approximation of γ^{a} at the same mole fraction x^{a}.

At the present time, the main problem resides in the determination of γ^{a}_{SL}. However, as suggested by Berti *et al.* (1999), it appears that in the case of zeolites a technique based on increments can be used to predict γ^{a}_{SL}. It is similar to the so-called UNIFAC technique proposed by Fredenslund *et al.* (1977) to estimate the activity coefficients in liquid mixtures. This type of approach must be developed, since an 'a priori' estimate of γ^{a}_{SL} will increase the accuracy of predictions of binary and possibly multiple vapour adsorption based on MPD.

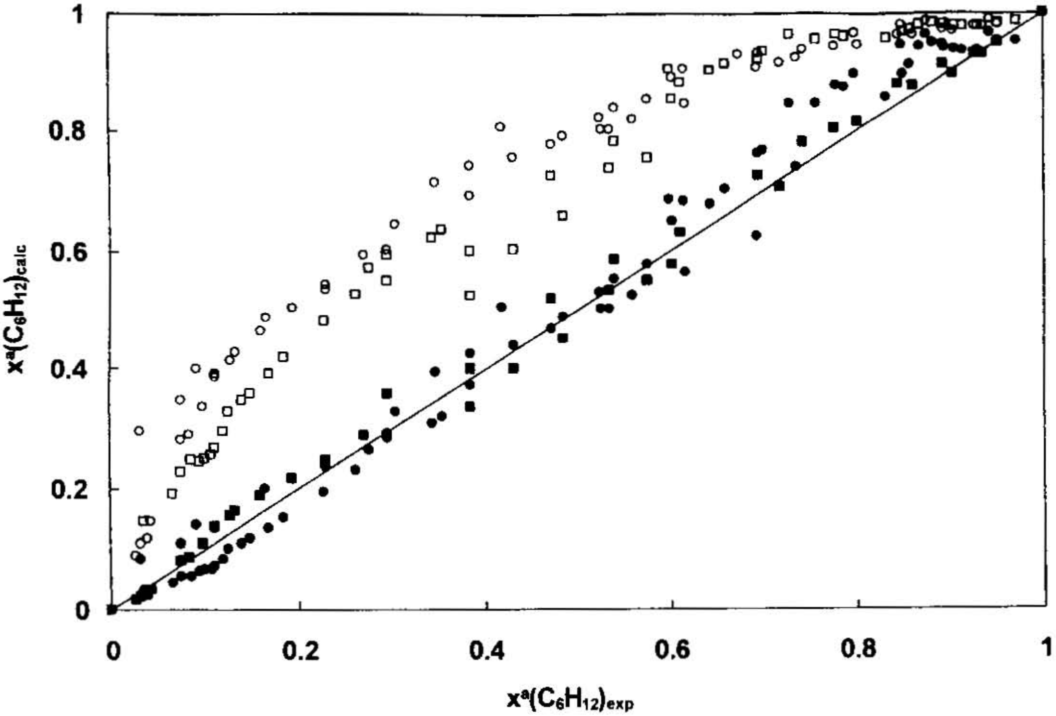

Figure 3. Correlation between the calculated and experimental mole fractions of cyclohexane vapours adsorbed with chlorobenzene on carbon U-03 at 293 K; $x^a(C_6H_{12})_{exp}$ obtained by GC-Headspace (□■) and quadrupole MS (○●); $x^a(C_6H_{12})_{calc}$ obtained from equations (1)–(3) assuming an ideal adsorbed state (□○) or using the activity coefficients γ^a_{LS} (■●).

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REFERENCES

Berti, C., Ulbig, P., Burdorf, A., Seippel, J. and Schulz, S. (1999) *Langmuir* **15**, 6035.

Blackburn, A., Kipling, J.J. and Tester, D.A. (1957) *J. Chem. Soc.* 2373.

Coulson, E.A., Hales, J.L. and Herrington, E.F.G. (1948) *Trans. Faraday Soc.* **44**, 636.

Dubinin, M.M. (1989) *Carbon* **27**, 457.

Fredenslund, A., Gmehling, J. and Rasmussen, P. (1977) *Vapor–Liquid Equilibria Using UNIFAC*, Elsevier, Amsterdam, Chap. 4.

Garrot, B. (2001) *PhD Thesis*, Université de Bourgogne, Dijon, France.

Gradshteyn, I.S. and Ryzhik, I.M. (1980) *Tables of Integrals, Series and Products*, Academic Press, New York, p. 940.

Guggenheim, E.A. (1967) *Thermodynamics*, North Holland, Amsterdam, pp. 191–205.

Lavanchy, A. and Stoeckli, F. (1997) *Carbon* **35**, 1573.

Lavanchy, A. and Stoeckli, F. (1999) *Carbon* **37**, 315.

Lavanchy, A., Stöckli, M., Wirz, C. and Stoeckli, F. (1996) *Adsorp. Sci. Technol.* **13**, 537.

Myers, A.L. and Prausnitz, J.M. (1965) *AIChE J.* **11**, 121.

Stoeckli, F. (1993) *Adsorp. Sci. Technol.* **10**, 3.

Stoeckli, F. (1995) in *Porosity in Carbons*, Patrick, J., Ed, Edward Arnold, London, pp. 67–92.

Stoeckli, F., Wintgens, D., Lavanchy, A. and Stöckli, M. (1997) *Adsorp. Sci. Technol.* **15**, 677.

Stoeckli, F., Couderc, G., Wintgens, D., Lavanchy, A. and Girardin, P. (2000) *Adsorp. Sci. Technol.* **18**, 581.

Valenzuela, D.P. and Myers, A.L. (1989) *Adsorption Equilibrium Data Handbook*, Prentice Hall, New York, pp. 3, 207 and 208.