

# Thermodynamics of Adsorption from Binary Liquid Mixtures on Heterogeneous Adsorbents

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The surface excess isotherms for adsorption of n-heptane–cyclohexane mixtures on graphon and benzene–cyclohexane mixtures on silica gel at three different temperatures have been analysed by a simple analytical model which accounts for the effects of the liquid-phase non-ideality, the dissimilarity of the adsorbate sizes and the adsorbent heterogeneity on the isotherm. The adsorbents are found to be substantially heterogeneous for these mixtures. An analytical expression for the heat of immersion of the heterogeneous adsorbent as a function of the equilibrium liquid-phase composition has been derived. It is shown that the adsorbent heterogeneity has a much more pronounced effect on the shape of the surface excess isotherm than on the heat of immersion.

The surface excess isotherm for adsorption of a binary liquid mixture on a solid adsorbent is affected by (a) the non-ideality of the liquid mixture, (b) the inequality of the adsorbate sizes, (c) the selectivity of adsorption and its variation with the composition of the liquid mixture and (d) the energetic heterogeneity of the adsorbent surface. A practical model must therefore include the effects of these variables. The monolayer-pore filling (MPF) model of adsorption<sup>1, 2</sup> with an ideal adsorbed phase provides a fundamental framework to describe the isotherm on an energetically homogeneous adsorbent. The model includes the effects of the variables (a)–(c) and gives an analytic expression for the isotherm. It is also possible to introduce a simple mathematical description of the surface heterogeneity into the theory and still obtain an analytical expression for the surface excess isotherm.<sup>2, 3</sup> It may be assumed that the heterogeneous adsorbent surface is composed of a distribution of homogeneous sites or patches and the overall isotherm is given by the integration of contributions of each site. Each homogeneous site can be described by the MPF model using a characteristic selectivity of adsorption for the site and a simple distribution of the site selectivities such as the uniform probability density function can be used to describe the heterogeneity. Since the detailed structure of the site selectivity distribution function is not critical,<sup>4</sup> this simple model may be adequate to describe the surface excess isotherms for most systems of practical interest. According to this model, the surface excess isotherm ( $n_1^e$ ) for component 1 of a binary liquid mixture is<sup>3</sup>

$$n_1^e = \frac{m_1}{(S_{0H} - S_{0L})} \left\{ \frac{x_2}{a_1} \left[ \left( \frac{S_H}{S_{0H}} \right)^{1/(\beta-1)} - \left( \frac{S_L}{S_{0L}} \right)^{1/(\beta-1)} \right] + \frac{a_2}{a_1(\beta-1)} \left( \frac{S_{0H}}{S_H} - \frac{S_{0L}}{S_L} \right) \right\} \quad (1)$$

where  $m_i$  is the specific (per unit weight) monolayer or pore filling adsorption capacity of the adsorbent for component  $i$  ( $i = 1, 2$ ) of the mixture.  $\beta$  is the ratio  $m_1/m_2$ .  $x_i$  and  $a_i$  ( $= x_i \gamma_i$ ) are, respectively, the bulk liquid phase mole fraction and activity of component  $i$ .  $\gamma_i$  is the activity coefficient of component  $i$  at  $x_i$ .  $S_{0L}$  and  $S_{0H}$  are, respectively, the lowest and the highest characteristic homogeneous site selectivities ( $S_0$ ) for adsorption of component 1 on the heterogeneous adsorbent.  $S_0$  is the site selectivity for component 1 at the limit of  $x_1 \rightarrow 0$ :

$$S_0 = \exp \left( \frac{A}{RTm_1} (\sigma_2^\circ - \sigma_1^\circ) \right) \quad S_{0L} \leq S_0 \leq S_{0H} \quad (2)$$

where  $(A\sigma_i^\circ)$  is the free energy of adsorption of pure liquid adsorbate  $i$  on a homogeneous site.  $R$  is the gas constant and  $T$  is the system temperature. The free energy of adsorption is a negative quantity. Component 1 is selectively adsorbed on the site when  $A(\sigma_2^\circ - \sigma_1^\circ) > 0$  or  $S_0 > 1$ .  $S_L$  and  $S_H$  are, respectively, the selectivities of component 1 on the sites characterized by  $S_{0L}$  and  $S_{0H}$  at a liquid-phase composition of  $x_1$ :<sup>3</sup>

$$S_H = S_{0H} (S_H a_1 + a_2)^{(\beta-1)/\beta} \quad (3)$$

$$S_L = S_{0L} (S_L a_1 + a_2)^{(\beta-1)/\beta}. \quad (4)$$

Eqn (3) and (4) explicitly relate  $S_H$  and  $S_L$  with, respectively,  $S_{0H}$  and  $S_{0L}$ . They show that the site selectivities can be strong functions of the liquid-phase composition when the adsorbates are dissimilar in sizes ( $\beta \neq 1$ ). The site selectivities are constant ( $S_H = S_{0H}$ ,  $S_L = S_{0L}$ ) only when  $\beta = 1$ .

The surface excess ( $n_i^e$ ) for component  $i$  of the mixture described by eqn (1) is defined by<sup>7</sup>

$$n_i^e = n' (x'_i - x_i)$$

where  $n'$  is the total number of moles adsorbed per unit weight of the adsorbent;  $x'_i$  and  $x_i$  are, respectively, the mole fractions of component  $i$  in the adsorbed and the equilibrium bulk liquid phases. According to this definition of the surface excess,  $\sum n_i^e = 0$ .

The integrated form of the Gibbs adsorption equation for the heterogeneous adsorbent gives<sup>1, 2</sup>

$$\frac{A}{RT} (\sigma_2^\circ - \sigma_1^\circ)^* = \int_0^1 \frac{n_1^e}{a_1 x_2} da_1 \quad (5)$$

where  $(A\sigma_i^\circ)^*$  is the free energy of adsorption of pure liquid adsorbate  $i$  on the heterogeneous adsorbent. Eqn (5) shows that the quantity  $(A/RT)(\sigma_2^\circ - \sigma_1^\circ)^*$  can be estimated from the experimental surface excess isotherm  $n_i^e(x_1)$ . Eqn (1) and (3)–(5) may be combined to get<sup>3</sup>

$$\frac{A}{RT} (\sigma_2^\circ - \sigma_1^\circ)^* = m_1 \left( \frac{S_{0H} \ln S_{0H} - S_{0L} \ln S_{0L}}{(S_{0H} - S_{0L})} - 1 \right). \quad (6)$$

Eqn (6) provides an explicit relationship between  $m_1$ ,  $S_{0H}$  and  $S_{0L}$ . Thus there are only three unknown variables in eqn (1), viz.  $m_1$ ,  $\beta$  and  $S_{0H}$  (or  $S_{0L}$ ). However,  $\beta$  is a function of the ratio of the liquid molar volumes ( $\bar{v}_i$ ) of the adsorbates for both non-porous and porous adsorbents<sup>5, 6</sup> in the absence of a molecular-sieving effect, where the larger molecules are excluded from the sites accessible to the smaller molecules. This reduces the number of adjustable parameters in eqn (1) to two. Furthermore, if the specific surface area ( $A$ ) or the specific pore volume ( $V$ ) of the adsorbent is known *a priori*,  $m_i$  can be obtained by  $m_i = A/\bar{a}_i$  for a non-porous adsorbent and by  $m_i = V/\bar{v}_i$  for a porous adsorbent where  $\bar{a}_i$  is the molar surface area for adsorption of the adsorbate  $i$ .  $m_i$  can also be independently measured from the pure-vapour isotherms of the adsorbates. In these cases there is only one adjustable parameter in eqn (1).

The key properties of the selectivity distribution function are the mean ( $\mu$ ) and dispersion ( $\sigma$ ), which are related to  $S_{0H}$  and  $S_{0L}$  by<sup>2, 3</sup>

$$\mu = (S_{0H} + S_{0L})/2 \quad (7)$$

$$\sigma = (S_{0H} - S_{0L})/2\sqrt{3}. \quad (8)$$

Eqn (7) and (8) show that  $S_{0H} = \mu(1 + \Psi)$  and  $S_{0L} = \mu(1 - \Psi)$ , where  $\Psi = \sqrt{3}(\sigma/\mu)$ . Thus eqn (1) and (6) can also be expressed in terms of  $m_1$ ,  $\beta$ ,  $\mu$  and  $\sigma$  (or  $\Psi$ ).

The temperature coefficient of  $(A\sigma_i^\circ)$  or  $(A\sigma_i^\circ)^*$  may be written as<sup>7</sup>

$$\frac{d}{dT} \left( \frac{A\sigma_i^\circ}{T} \right) = \frac{Q_i}{T^2} \quad (9)$$

$$\frac{d}{dT} \left( \frac{A\sigma_i^\circ}{T} \right)^* = \frac{Q_i^*}{T^2} \quad (10)$$

where  $Q_i$  and  $Q_i^*$  are, respectively, the heat of immersion of a homogeneous adsorbent of characteristic site selectivity  $S_0$  [eqn (2)] and that for the heterogeneous adsorbent into the pure liquid adsorbate  $i$ . The  $Q_i$  are positive quantities. It follows from eqn (2) and (9) that

$$\frac{d \ln S_0}{dT} = \frac{(Q_2 - Q_1)}{m_1 RT^2} - (\ln S_0) \frac{d \ln m_1}{dT}. \quad (11)$$

The second term on the right-hand side of eqn (11) is usually very small compared to the first term because  $m_i$  (or  $\bar{v}_i$ ) is generally a very weak function of  $T$ . Thus

$$\frac{d \ln S_0}{dT} \approx \frac{Q_2 - Q_1}{m_1 RT^2}. \quad (12)$$

Eqn (6) can be differentiated with respect to  $T$  and combined with eqn (7)–(10) and (12) to get

$$E^* \approx E_H \frac{1+\Psi}{4\Psi^2} \left[ 2\Psi - (1-\Psi) \ln \left( \frac{1+\Psi}{1-\Psi} \right) \right] - E_L \frac{1-\Psi}{4\Psi^2} \left[ 2\Psi - (1+\Psi) \ln \left( \frac{1+\Psi}{1-\Psi} \right) \right] \quad (13)$$

where  $E^* = (Q_2^* - Q_1^*)$ ,  $E_H = (Q_2 - Q_1)_H$  and  $E_L = (Q_2 - Q_1)_L$ . The subscripts H and L represent homogeneous sites with limiting selectivities of  $S_{0H}$  and  $S_{0L}$ . The heats of immersions ( $Q_i$ ,  $Q_i^*$ ,  $E$  or  $E^*$ ) are usually weak functions of  $T$ . Therefore, eqn (13) shows that the parameter  $\Psi$  (or  $\sigma/\mu$ ) is also a weak function of  $T$ . In other words, the ratio of the dispersion to the mean of the selectivity distribution function may be considered to be temperature independent.

## Discussion

### Analysis of Experimental Data

The model described above was used to interpret the isotherm data for adsorption of (a) n-heptane (1)–cyclohexane (2) mixtures on graphon<sup>8</sup> and (b) benzene (1)–cyclohexane (2) mixtures on silica gel<sup>7</sup> at three different temperatures. The graphon was a non-porous adsorbent with a B.E.T. surface area ( $A$ ) of  $86 \text{ m}^2 \text{ g}^{-1}$ .<sup>8</sup> The silica gel was a porous adsorbent with a mean pore diameter of  $22 \text{ \AA}$ .<sup>7</sup> The liquid mixture for system (a) was nearly ideal ( $a_i = x_i$ ). The system (b) was non-ideal and the activity coefficients ( $\gamma_i$ ) at various temperatures were estimated from the available data at 313 and 343 K<sup>9</sup> by assuming that  $[\partial \ln \gamma_i / \partial T]_{x_i}$  was independent of  $T$ . The monolayer capacities of the adsorbates for system (a) were calculated using the B.E.T. area of the graphon and the  $\bar{a}_i$  values obtained by the method of McClellan and Harnsberger.<sup>5</sup> The pore-filling capacities of the silica gel for the adsorbate of system (b) were obtained from their saturation capacities for adsorption of pure vapours at 303 K<sup>9</sup> and by using the Gurvitch rule.<sup>6</sup> The quantities  $(A/RT)(\sigma_2^\circ - \sigma_1^\circ)^*$  for each system at different temperatures were obtained by eqn (5) using the experimental isotherms. The remaining parameter ( $S_{0H}$  or  $S_{0L}$ ) of eqn (1) was then estimated by a trial-and-error procedure.  $\Psi$  was assumed to be temperature-independent as discussed earlier. A desk-top calculator was used. Tables 1 and 2 summarize the model parameters.

**Table 1.** Model parameters for adsorption of n-heptane (1) and cyclohexane (2) mixtures on Graphon

parameter	283 K	323 K	343 K
$m_1$	0.237 <sup>a</sup>	0.228	0.222
$\beta$	0.786	0.786	0.786
$S_{0H}$	5.703	3.985	3.125
$S_{0L}$	0.634	0.443	0.347
$\mu$	3.168	2.214	1.736
$\Psi$	0.80	0.80	0.80
$f$	0.072	0.157	0.235
$(A/RT)(\sigma_2^\circ - \sigma_1^\circ)^*$	0.241 <sup>a</sup>	0.150	0.092
$(A/RT)(\sigma_2^\circ - \sigma_1^\circ)_H$	0.413	0.315	0.253
$(A/RT)(\sigma_2^\circ - \sigma_1^\circ)_L$	-0.108	-0.186	-0.235

<sup>a</sup> In mmol g<sup>-1</sup>.**Table 2.** Model parameters for adsorption of benzene (1) and cyclohexane (2) mixtures on silica gel

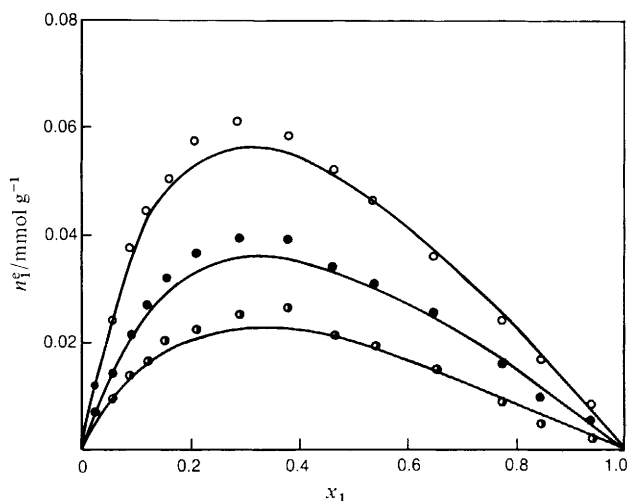
parameter	273 K	303 K	333 K
$m_1$	4.05 <sup>a</sup>	3.91	3.76
$\beta$	1.28	1.28	1.28
$S_{0H}$	16.630	12.480	9.840
$S_{0L}$	0.415	0.311	0.246
$\mu$	8.526	6.398	5.044
$\Psi$	0.9513	0.9513	0.9513
$f$	0.036	0.057	0.078
$(A/RT)(\sigma_2^\circ - \sigma_1^\circ)^*$	7.72 <sup>a</sup>	6.63	5.19
$(A/RT)(\sigma_2^\circ - \sigma_1^\circ)_H$	11.38	9.87	8.60
$(A/RT)(\sigma_2^\circ - \sigma_1^\circ)_L$	-3.56	-4.57	-5.27

<sup>a</sup> In mmol g<sup>-1</sup>.

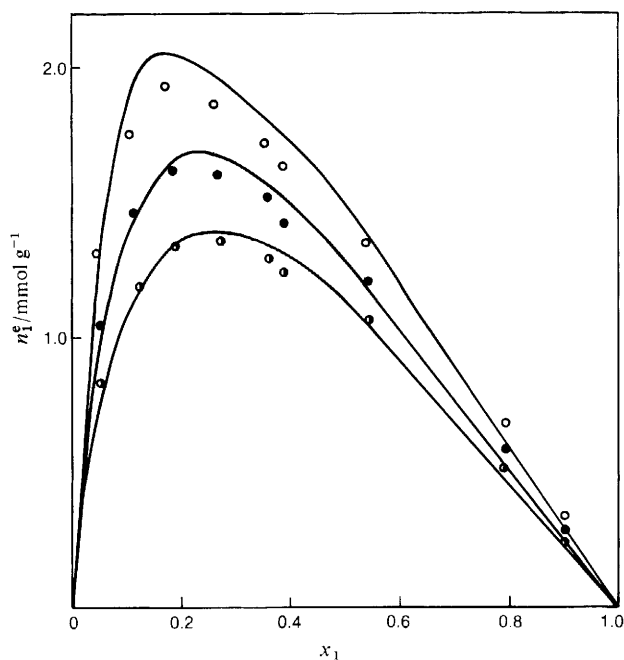
Fig. 1 and 2, respectively, show the experimental isotherms (circles) for system (a) at 283, 323 and 343 K and system (b) at 273, 303 and 333 K. The isotherms are U-shaped in all cases, indicating that the component 1 is selectively adsorbed on the adsorbents at all  $x_1$ . The solid lines in the figures represent the best fit of the data by eqn (1) using the parameters of tables 1 and 2. Eqn (1) describes the data very well for both systems at all temperatures. The agreement between experiment and theory is generally better than  $\pm 5\%$ , except in the region of  $0.2 < x_1 < 0.4$ , where the model underpredicts the  $n_1^e$  for system (a) and overpredicts the  $n_1^e$  for system (b) but not more than 10% in either case.

The Systems (a) and (b) are significantly different. One adsorbent is non-porous and the other is highly porous. The  $\beta$  for system (a) is less than unity but that for system (b) is larger than unity. The quantity  $(A/RT)(\sigma_2^\circ - \sigma_1^\circ)^*$  is very small for system (a); that for case (b) is at least an order of magnitude larger. It may therefore be concluded that eqn (1) is capable of describing the surface excess isotherms for a variety of adsorption systems.

Tables 1 and 2 show that system (a) has lower values of  $\mu$  and  $\Psi$  than those for system (b). The parameter  $\Psi$  is a measurement of the degree of heterogeneity.  $\Psi \rightarrow 0$  ( $S_{0L} = S_{0H}$ )



**Fig. 1.** Surface excess isotherms for adsorption of n-heptane (1)–cyclohexane (2) mixtures on Graphon: (—) theory; experiment: ○, 283; ●, 323 and ◐, 343 K.



**Fig. 2.** Surface excess isotherms for adsorption of benzene (1)–cyclohexane (2) mixtures on silica gel: (—) theory; experiment: ○, 273; ●, 303 and ◐, 333 K.

represents a homogeneous adsorbent.  $\Psi \rightarrow 1$  represents the maximum possible heterogeneity by the uniform distribution model because  $S_{0L} \rightarrow 0$  under that condition. This corresponds to a site of infinite selectivity for component 2 as the lower limit of  $S_0$ . Thus the model shows that the graphon is relatively less heterogeneous for adsorption of system (a) than the silica gel for adsorption of system (b). The lower value of  $\mu$  for system (a) indicates that, on average, n-heptane is less selectively adsorbed from cyclohexane on

**Table 3.** Heats of immersion

system	$E_L$	$E_H$	$E^*$
(a) n-heptane (1)–cyclohexane (2) on Graphon	–0.42 <sup>a</sup>	–0.52	–0.445
(b) benzene (1)–cyclohexane (2) on silica gel	–5.08	–8.30	–7.59

<sup>a</sup> In cal g<sup>–1</sup> (1 cal = 4.184 J).

the graphon that adsorption of benzene from cyclohexane on the silica gel. Both systems, however, have significant spreads ( $S_{0H} - S_{0L}$ ) in the site selectivities. The  $S_{0L}$  values for both systems are less than unity indicating that a certain fraction of the homogeneous sites on both adsorbents are selective towards component 2 of the mixtures at all temperatures of this study. The cumulative fraction of sites ( $f$ ) having  $S_0 < 1$  ( $S_0 = 1$  represents a non-selective site) may be obtained for the uniform site selectivity distribution by

$$f = \frac{1 - S_{0L}}{S_{0H} - S_{0L}}. \quad (14)$$

Tables 1 and 2 show that  $f$  for system (a) is larger than that for system (b) at all temperatures. The absolute values of  $f$  for both systems are, however, small and the fraction of sites selective towards component 1,  $(1 - f)$ , dominate on both adsorbents.

Tables 1 and 2 also show that  $S_{0H}$  and  $S_{0L}$  for both systems decrease with increasing  $T$ . Thus, according to eqn (12),  $E_H$  and  $E_L$  are negative quantities. In other words the heat of immersion of pure component 1 is larger than that of pure component 2 for all the sites of these systems. The exact magnitude of  $E_H$  and  $E_L$  were obtained by calculating  $(A/RT)(\sigma_2^0 - \sigma_1^0)$  for the  $S_{0H}$  and the  $S_{0L}$  sites at different temperatures using eqn (2) (see tables 1 and 2) and they by plotting  $[(A/RT)(\sigma_2^0 - \sigma_1^0)]$  against  $1/T$ . The slopes of these lines according to eqn (9), are equal to  $-E/R$  for the appropriate sites. The  $E$  values are given in table 3 along with the values of  $E^*$  for the systems obtained in a similar fashion using eqn (10). It may be seen from table 3 that the difference between  $E_L$  and  $E_H$  for system (a) is much smaller than that for system (b). This difference is also a measure of the degree of heterogeneity of the adsorbent in terms of the site distribution of the relative heats of immersions of the pure adsorbates instead of the distribution of site selectivities of adsorption.  $E_L = E_H$  for a homogeneous adsorbent. The results are consistent in either language. The data also show that  $f$  increases with increasing  $T$  for both systems. More sites become selective towards component 2 of either system as the system temperature is increased.

### Heat of Immersion

Besides the surface excess isotherm, the only other thermodynamic property of the binary liquid adsorption system that can be measured directly is the specific heat of immersion of the adsorbent into the liquid mixture. The heat can be measured calorimetrically. Like  $n_1^e$ , the heat of immersion depends on  $a_i$ ,  $\beta$  and the adsorbent heterogeneity. An analytic expression for the heat of immersion can also be derived for a heterogeneous adsorbent using the model discussed above. For simplicity, we will consider the adsorption from an ideal binary liquid mixture only. The surface excess isotherm  $(n_1^e)_h$  for component 1 of such a mixture on a homogeneous site is given by the MPF model with an ideal adsorbed phase as<sup>1, 2</sup>

$$(n_1^e)_h = \frac{m_1 x_1 x_2 (S - 1)}{S x_1 + \beta x_2} \quad (15)$$

where  $S$  is the selectivity of adsorption of component 1 on the site at a liquid-phase composition of  $x_1$ :

$$S = S_0(Sx_1 + x_2)^{(\beta-1)/\beta}. \quad (16)$$

$S_0$  is the characteristic limiting selectivity for the homogeneous site defined by eqn (2). Eqn (15) and (16) are limiting forms of eqn (1) and (3) or (4), respectively, for adsorption of an ideal liquid mixture ( $a_i = x_i$ ) on a homogeneous adsorbent [ $S_{0H} = S_{0L} = S_0$ ].

The heat of immersion ( $Q$ ) of an ideal binary liquid mixture of composition  $x_1$  is thermodynamically related to  $(n_1^e)_h$  by<sup>7</sup>

$$\left(\frac{\partial[n_1^e]_h}{\partial T}\right)_{x_1} = -\frac{x_1 x_2}{RT^2} \left(\frac{\partial Q}{\partial x_1}\right)_T. \quad (17)$$

Eqn (15) and (16) can be differentiated with respect to  $T$  at constant  $x_i$  to obtain an analytic expression for  $(\partial n_1^e / \partial T)_{x_1}$  which can be substituted into eqn (17) and integrated to get

$$F = \frac{Q - Q_2}{Q_1 - Q_2} = \frac{Sx_1}{Sx_1 + \beta x_2}. \quad (18)$$

It is assumed in the derivation of eqn (18) that  $m_i$  is not a function of  $T$ .

Eqn (16) and (18) provide an analytic expression for the dimensionless heat of immersion [ $F = (Q - Q_2)/(Q_1 - Q_2)$ ] of a homogeneous adsorbent characterized by  $S_0$ . It describes the functional dependence of  $Q$  on  $\beta$ ,  $S_0$  and  $x_1$ . A limiting form of eqn (18) for the special case of  $\beta = 1$  ( $S = S_0$ ) was previously derived.<sup>7</sup>

The dimensionless heat of immersion [ $F^* = (Q^* - Q_2^*)/(Q_1^* - Q_2^*)$ ] for a heterogeneous adsorbent can then be obtained by the integration of contributions of each site using the uniform probability density function,  $\lambda(S_0) = 1/(S_{0H} - S_{0L})$ , for the distribution of the site selectivities:

$$F^* = \int_{S_{0L}}^{S_{0H}} F \lambda(S_0) dS_0. \quad (19)$$

Eqn (18) can be substituted into eqn (19) and integrated with the help of eqn (16) to get

$$F^* = \frac{1}{x_1(S_{0H} - S_{0L})} \left[ \left(\frac{S_H}{S_{0H}}\right)^{1/(\beta-1)} - \left(\frac{S_L}{S_{0L}}\right)^{1/(\beta-1)} + \frac{x_2}{(\beta-1)} \left(\frac{S_{0H}}{S_H} - \frac{S_{0L}}{S_L}\right) \right]. \quad (20)$$

Eqn (20) is the analytic expression for the heat of immersion of a heterogeneous adsorbent into an ideal binary liquid mixture of composition  $x_i$ . The corresponding surface excess isotherm for component 1 is given by eqn (1) with  $a_i = x_i$ .  $S_H$  and  $S_L$  in eqn (20) are given by eqn (3) and (4), respectively.

Eqn (20) has the correct limiting values. It can be shown by using L'hôpital's rule that  $F^* \rightarrow 0$  as  $x_1 \rightarrow 0$  ( $S_H \rightarrow S_{0H}$ ,  $S_L \rightarrow S_{0L}$ ). On the other hand, it is easy to show that  $F^* \rightarrow 1$  as  $x_1 \rightarrow 1$  [ $S_H \rightarrow (S_{0H})^\beta$ ,  $S_L \rightarrow (S_{0L})^\beta$ ].

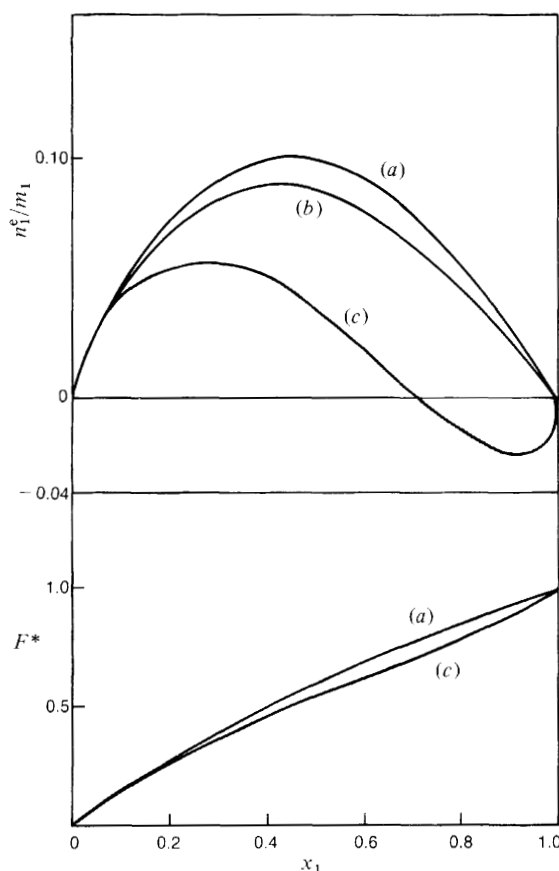
Eqn (20) shows that  $F^*(x_1)$  is a function of  $\beta$ ,  $S_{0H}$  and  $S_{0L}$ . It can also be expressed in terms of  $\beta$ ,  $\mu$  and  $\sigma$  (or  $\Psi$ ). The limiting slopes of the function  $F^*(x_1)$  are

$$\left(\frac{\partial F^*}{\partial x_1}\right)_{T, x_1 \rightarrow 0} = \frac{\mu}{\beta} \quad (21)$$

$$\left(\frac{\partial F^*}{\partial x_1}\right)_{T, x_1 \rightarrow 1} = \frac{\beta}{2(1-\beta)\mu^\beta} \frac{(1+\Psi)^{1-\beta} - (1-\Psi)^{1-\beta}}{\Psi}. \quad (22)$$

Eqn (21) shows that the slope of the  $F^*(x_1)$  curve at the limit of  $x_1 \rightarrow 0$  is a function of the mean of the distribution only. It is independent of the degree of heterogeneity ( $\Psi$ ) of the adsorbent. Eqn (18) has the same limiting slope which can be derived by using eqn (16) and setting ( $\mu = S_0$ ). On the other hand, eqn (22) shows that the limiting slope





**Fig. 3.** Effect of adsorbent heterogeneity on  $n_1^e$  and  $F^*$  for  $\mu = 1.5$ ,  $\beta = 1.0$ .  $\Psi =$  (a) 0, (b) 0.5 and (c) 1.0.

of  $F^*(x_1)$  at  $x_1 \rightarrow 1$  is dependent on both  $\mu$  and  $\Psi$ . The corresponding slope for a homogeneous adsorbent can be obtained from eqn (16) and (18) or by applying the limit of  $\Psi \rightarrow 0$  to eqn (22):

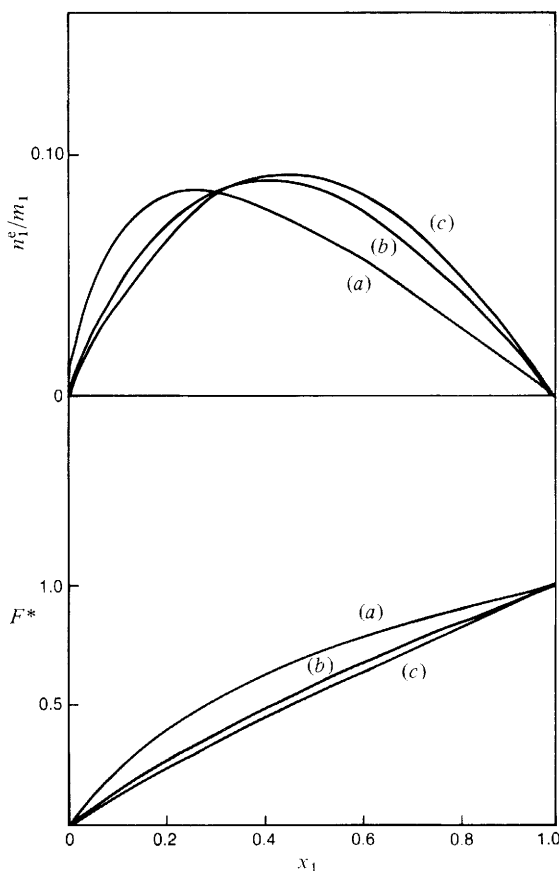
$$\left(\frac{\partial F}{\partial x_1}\right)_{T; x_1 \rightarrow 1} = \left(\frac{\partial F^*}{\partial x_1}\right)_{T; x_1 \rightarrow 1, \Psi \rightarrow 0} = \frac{\beta}{\mu^\beta}. \quad (23)$$

These results indicate that the shape of the dimensionless heat of immersion curve is similar for a homogeneous or a heterogeneous adsorbent in the low- $x_1$  region when  $\mu = S_0$ . The effect of heterogeneity on the heat of immersion becomes apparent in the high- $x_1$  region only. Similar behaviour is also exhibited by the surface excess isotherms.<sup>2, 3</sup> The following parametric study elaborates on these points.

### Parametric Study

Fig. 3 shows the shapes of the surface excess isotherms and the dimensionless heat of immersion curves for a homogeneous ( $\Psi = 0$ ) and a heterogeneous adsorbent ( $\Psi = 0.5, 1.0$ ). They are generated using eqn (24) and (25) and the same values of  $\mu = 1.5$  and  $\beta = 1.0$ . Adsorbent heterogeneity has a drastic effect on the  $n_1^e(x_1)$  plot. The homogeneous isotherm has a U shape which changes to an S-shaped isotherm when the





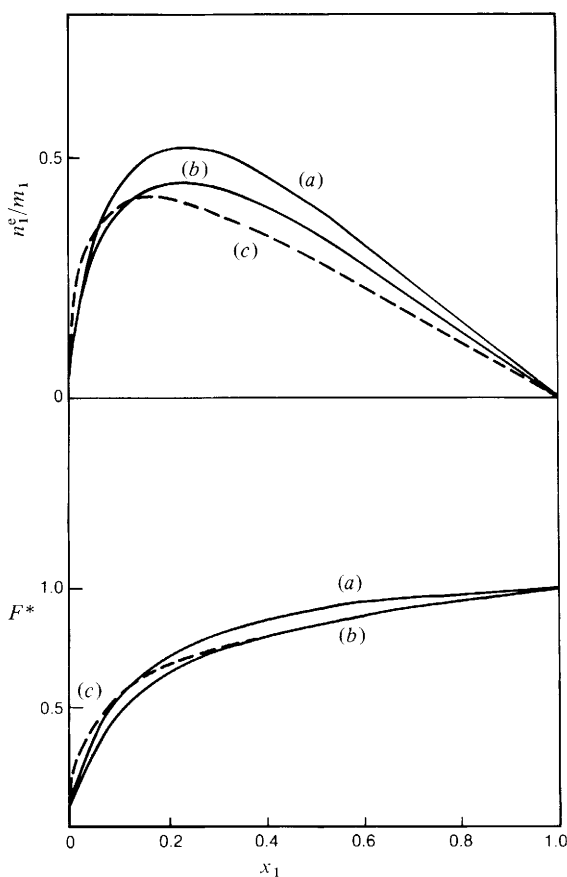
**Fig. 4.** Effect of adsorbate sizes on  $n_1^e$  and  $F^*$  for  $\mu = 1.5$ ,  $\Psi = 0.5$ .  $\beta = (a) 0.5$ ,  $(b) 1.0$  and  $(c) 1.25$ .

adsorbent is substantially heterogeneous. However,  $F^*(x_1)$  does not differ significantly from  $F(x_1)$  even when  $\Psi \rightarrow 1$ . The slight difference between the two curves is exhibited in the high- $x_1$  region where  $F^*(x_1) < F(x_1)$ .

Fig. 4 shows the effect of  $\beta$  on  $n_1^e(x_1)$  and  $F^*(x_1)$  for a given  $\mu = 1.5$  and  $\Psi = 0.5$ . The effect of  $\beta$  is more pronounced on  $n_1^e(x_1)$  than on  $F^*(x_1)$ . However,  $F^*(x_1)$  for a given  $x_1$  increases as  $\beta$  decreases.

Fig. 5 plots the  $n_1^e(x_1)$  and the  $F^*(x_1)$  curves for a high value of  $\mu = 10.0$  and various combinations of  $\beta$  and  $\Psi$ . It shows that the effect of the adsorbent heterogeneity on  $n_1^e(x_1)$  is less pronounced when  $\mu$  is large.  $F^*(x_1)$  is also little affected by the variations in  $\beta$  or  $\Psi$  as before. The important feature of fig. 5 is that the slope of  $F^*(x_1)$  curve in the high- $x_1$  region is very small. This result follows from eqn (22) and (23) which show that  $(\partial F^*/\partial x_1)_{x_1 \rightarrow 1} \rightarrow 0$  as  $\mu \rightarrow \infty$ . This type of behaviour has been experimentally measured for many systems.<sup>10</sup>

An obvious conclusion from the above study is that the heat of immersion may not be a sensitive variable for estimation of the degree of heterogeneity of an adsorbent. Analysis of the surface excess isotherm by a heterogeneous model is required for this purpose.



**Fig. 5.** Effect of  $\beta$  and  $\Psi$  on  $n_1^e$  and  $F^*$  at  $\mu = 10.0$ . (a)  $\beta = 1.0$ ,  $\Psi = 0$ ; (b)  $\beta = 1.0$ ;  $\Psi = 1$ ; (c)  $\beta = 0.5$ ;  $\Psi = 1$ .

### Special Case of $\beta = 1$ ( $m_i = m$ )

For the special case of adsorption from an ideal binary liquid mixture of equal adsorbate sizes, eqn (1), (20), (21) and (22) reduce to

$$n_1^e = m \left[ x_2 - \frac{x_2}{x_1(S_{0H} - S_{0L})} \ln \left( \frac{S_{0H} x_1 + x_2}{S_{0L} x_1 + x_2} \right) \right] \quad (24)$$

$$F^* = 1 - \frac{x_2}{x_1(S_{0H} - S_{0L})} \ln \left( \frac{S_{0H} x_1 + x_2}{S_{0L} x_1 + x_2} \right) \quad (25)$$

$$\left( \frac{\partial F^*}{\partial x_1} \right)_{T; x_1 \rightarrow 0} = \mu \quad (26)$$

$$\left( \frac{\partial F^*}{\partial x_1} \right)_{T; x_1 \rightarrow 1} = \frac{1}{2\mu\Psi} \ln \left( \frac{1+\Psi}{1-\Psi} \right). \quad (27)$$

## Conclusions

It may be concluded that the simple analytical model of surface excess isotherm, eqn (1), is capable of describing isotherms for adsorption of various binary liquid mixtures on energetically heterogeneous adsorbents. The model can describe both the U- and the S-shaped isotherms and provides significant insight into the thermodynamic nature of the adsorbent surface. An analytical expression for the heat of immersion of the adsorbent as a function of the liquid-phase composition, eqn (20), can also be derived using the model. The adsorbent heterogeneity has a much more pronounced effect on the shape of the surface excess isotherm than on the heat of immersion.

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