Supplementary Material (ESI) for PCCP

Supplementary

A site energy distribution function from Toth isotherm for adsorption of gases on heterogeneous surfaces

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Derivation of site energy distribution function based on a Toth isothem (Type 1) by condensation approximation method

The Toth isotherm involving three parameters is given by: [1-2]

$$q_e = \frac{q_m p}{\left(b + p^t\right)^{1/t}} \qquad (1)$$

where, q_e is the amount adsorbed at equilibrium, q_m is the maximum adsorption capacity, b is a constant related to the binding affinity and is specific to adsorbate-adsorbent pairs and t is the Toth isotherm exponent related to surface heterogeneity, usually less than or equal to unity. The t equal to unity suggests a homogeneous adsorption process.

For convenience of determining the site energy distribution, let us replace q_m by a.

The site energy distribution function, $f(E^*)$ according to a *condensation approximation* method is given by [3]

$$f(E^*) = -dq_e(E^*)/dE^* \qquad (2)$$

The site energy distribution of an adsorbent material based on Toth isotherm can be obtained by differentiating local isotherm applied with respect to E^*

The equilibrium pressure in eq (1) can be related to the energy of adsorption using the Polanyi potential theory given by [3,4]

$$p = p_s \exp\left(-\frac{E^*}{RT}\right) = p_s \exp\left(-\frac{E - E_s}{RT}\right) \qquad (3)$$

The E_s reference state for E represents the lowest physically realizable sorption energy, and its magnitude depends only on the solute and is independent of the adsorbent [4].

substituting eq (3) in (1) we get

$$amount.adsorbed = \frac{ap_s \exp\left(-\frac{E^*}{RT}\right)}{\left(b + \left(p_s \exp\left(-\frac{E^*}{RT}\right)\right)^t\right)^{1/t}} \qquad (4)$$

for convenience, let us rewrite, $-E^* = x$, $p = p_s$ and $RT = r$, thus eq (4) can be written as:

$$amount.adsorbed = \frac{ap\exp\left(-\frac{x}{r}\right)}{\left(b+\left(p\exp\left(-\frac{x}{r}\right)\right)^{t}\right)^{1/t}} \qquad (5)$$

substituting eq(5) in (4), the site energy distribution function can be written as:

$$f(x) = \frac{d}{dx}\left(pa\exp\left(-\frac{x}{r}\right)\left(b+\left(p\exp\left(-\frac{x}{r}\right)\right)^{t}\right)^{-1/t}\right) \qquad (6)$$

Let $u = \exp(-x/r)$ and $v = \left(b+\left(p\exp\left(-\frac{x}{r}\right)\right)^{t}\right)^{-1/t}$, then from the product rule: $\frac{d(uv)}{dx} = \frac{du}{dx}v + u\frac{dv}{dx}$, we get

$$= pa\left(b+\left(p\exp\left(-\frac{x}{r}\right)\right)^{t}\right)^{-1/t}\frac{d}{dx}\left(\exp\left(-\frac{x}{r}\right)\right) + \exp\left(-\frac{x}{r}\right)\frac{d}{dx}\left(\left(b+\left(p\exp\left(-\frac{x}{r}\right)\right)^{t}\right)^{-1/t}\right) \qquad (7)$$

if $u = -x/r$, then applying the chain rule of differentiation, $\frac{de^{u}}{dx} = e^{u}\frac{du}{dx}$, and applying the rule: $d(x^{n}) = nx^{n-1}$, we get

$$= pa\left(\exp\left(-\frac{x}{r}\right)\frac{d}{dx}\left(b+\left(p\exp\left(-\frac{x}{r}\right)\right)^{t}\right)\right)^{-1/t} - \frac{\exp\left(-\frac{x}{r}\right)\left(\left(b+\left(p\exp\left(-\frac{x}{r}\right)\right)^{t}\right)^{-1/t}\right)}{r}$$

Let $u=-x/r$, then by applying the chain rule, we get

$$= pa\left(p\left(-\exp\left(-\frac{2x}{r}\right)\left(p\exp\left(-\frac{x}{r}\right)\right)^{t-1}\right)\left(b+\left(p\exp\left(-\frac{x}{r}\right)\right)t\right)^{-\frac{1}{t}-1}\frac{d}{dx}\left(-\frac{x}{r}\right)\right) - \frac{\exp\left(-\frac{x}{r}\right)\left(\left(b+\left(p\exp\left(-\frac{x}{r}\right)\right)^{t}\right)^{-1/t}\right)}{r}$$

Applying the rule: $d(x^{n}) = nx^{n-1}$, the above equation can be further simplified to

$$f\left(E^{*}\right) = -bpa\exp\left(-\frac{x}{r}\right)\left(b+\left(p\exp\left(-\frac{x}{r}\right)\right)^{t}\right)^{-\frac{t+1}{t}} \qquad (8)$$

Replacing the parameters: *x =E*, p = pS, r = RT, and a = q,* the site energy distribution function following a Toth isotherm explained in eq (1) is given by:

$$f\left(E^*\right) = -bp_s q \exp\left(-\frac{E^*}{RT}\right)\left(b + \left(p_s \exp\left(-\frac{E^*}{r}\right)\right)^t\right)^{-\frac{t+1}{t}} \quad (9)$$

Derivation of site energy distribution function based on a Toth isothem (Type 2) by condensation approximation method

The Toth isotherm involving three parameters is given by: [1-2]

$$q_e = \frac{q_m bp}{\left(1 + (bp)^t\right)^{1/t}} \quad (1)$$

where, q_{m} is the maximum adsorption capacity, b is a constant related to the binding affinity and is specific to adsorbate-adsorbent pairs and t is the Toth isotherm exponent related to surface heterogeneity, usually less than or equal to unity. The t equal to unity suggests a homogeneous adsorption process. For convenience, let us replace q_{m} by q.

The site energy distribution function, $f(E^*)$ is given by [3]

$$f(E^*) = -dq_e(E^*)/dE^* \qquad (2)$$

The site energy distribution of an adsorbent material based on Toth isotherm can be obtained by differentiating local isotherm applied with respect to E^*

The equilibrium pressure in eq (1) can be related to the energy of adsorption using the Polanyi potential theory given by [3-4]

$$p = p_s \exp\left(-\frac{E^*}{RT}\right) = p_s \exp\left(-\frac{E - E_s}{RT}\right) \qquad (3)$$

substituting eq (3) in (1) we get

$$amount.adsorbed = \frac{q_m b p_s \exp\left(-\frac{E^*}{RT}\right)}{\left(1+\left(bp_s \exp\left(-\frac{E^*}{RT}\right)\right)^t\right)^{1/t}} \qquad (4)$$

for convenience, let us rewrite, $-E^* = x$, $p_s = p$, $q_m = a$ and $RT = r$, thus eq (4) can be written as:

$$amount.adsorbed = \frac{abp \exp\left(-\frac{x}{r}\right)}{\left(1+\left(bp \exp\left(-\frac{x}{r}\right)\right)^t\right)^{1/t}} \qquad (5)$$

substituting eq(5) in (4), the site energy distribution function can be written as:

$$f(x) = \frac{d}{dx}\left(bpa \exp\left(-\frac{x}{r}\right)\left(\left(bp \exp\left(-\frac{x}{r}\right)\right)^t + 1\right)^{-1/t}\right) \qquad (6)$$

let u = exp(-x/r) and $v=\left(\left(bp\exp\left(-\frac{x}{r}\right)\right)^{t}+1\right)^{-1/t}$, then from the product rule: $\frac{d(uv)}{dx}=\frac{du}{dx}v+u\frac{dv}{dx}$, we get

$$=bpa\left(\left(\left(bp\exp\left(-\frac{x}{r}\right)\right)^{t}+1\right)^{-1/t}\frac{d}{dx}\left(\exp\left(-\frac{x}{r}\right)\right)+\exp\left(-\frac{x}{r}\right)\frac{d}{dx}\left(\left(\left(bp\exp\left(-\frac{x}{r}\right)\right)^{t}+1\right)^{-1/t}\right)\right) \quad (7)$$

Let, u = -x/r , then applying the chain rule of differentiation $\frac{de^{u}}{dx}=e^{u}\frac{du}{dx}$,we get

$$=bpa\left(\exp\left(-\frac{x}{r}\right)\left(\left(bp\exp\left(-\frac{x}{r}\right)\right)^{t}+1\right)^{-1/t}\frac{d}{dx}\left(-\frac{x}{r}\right)+\exp\left(-\frac{x}{r}\right)\frac{d}{dx}\left(\left(\left(bp\exp\left(-\frac{x}{r}\right)\right)^{t}+1\right)^{-1/t}\right)\right) \quad (8)$$

Since, d(x^{n}) = nx^{n-1}, the above equation can be modified as

$$= bpa\left(\exp\left(-\frac{x}{r}\right)\frac{d}{dx}\left(\left(\left(bp\exp\left(-\frac{x}{r}\right)\right)^{t}+1\right)^{-1/t}\right) + \frac{\exp\left(-\frac{x}{r}\right)\left(\left(\left(bp\exp\left(-\frac{x}{r}\right)\right)^{t}\right)+1\right)^{-1/t}}{r} \right) \tag{9}$$

For convenience, let $u = \left(bp\exp\left(-\frac{x}{r}\right)\right)^{t} + 1$ and $n = -1/t$, then using the chain rule of differentiation, $\frac{du^{n}}{dx} = nu^{n-1}\frac{du}{dx}$, and simplifying the resulting expression, we get

$$= bpa\left(-\frac{\exp\left(-\frac{x}{r}\right)\left(\left(bp\exp\left(-\frac{x}{r}\right)\right)^{t}+1\right)^{-\frac{1}{t}-1}}{t}\frac{d}{dx}\left(\left(bp\exp\left(-\frac{x}{r}\right)\right)^{t}\right) - \frac{\exp\left(-\frac{x}{r}\right)\left(\left(\left(bp\exp\left(-\frac{x}{r}\right)\right)^{t}\right)+1\right)^{-1/t}}{r} \right) \tag{10}$$

if $u = bp\exp(-x/r)$ and $n = t$, then using the chain rule, $\frac{du^{n}}{dx} = nu^{n-1}\frac{du}{dx}$, we get

$$= bpa\left(-bp\exp\left(-\frac{x}{r}\right)\left(bp\exp\left(-\frac{x}{r}\right)\right)^{t-1}\left(\left(bp\exp\left(-\frac{x}{r}\right)\right)^{t}+1\right)^{-\frac{1}{t}-1}\frac{d}{dx}\exp\left(-\frac{x}{r}\right) - \frac{\exp\left(-\frac{x}{r}\right)\left(\left(\left(bp\exp\left(-\frac{x}{r}\right)\right)^{t}+1\right)^{-1/t}\right)}{r} \right) \quad (11)$$

if $u = -x/r$, the applying the chain rule $\frac{de^u}{dx} = e^u\frac{du}{dx}$, we get

$$= bpa\left(-\frac{bp\exp\left(-\frac{2x}{r}\right)\left(bp\exp\left(-\frac{x}{r}\right)\right)^{t-1}\left(\left(bp\exp\left(-\frac{x}{r}\right)\right)^{t}+1\right)^{-\frac{1}{t}-1}}{r}\frac{d}{dx}(x) - \frac{\exp\left(-\frac{x}{r}\right)\left(\left(\left(bp\exp\left(-\frac{x}{r}\right)\right)^{t}+1\right)^{-1/t}\right)}{r} \right) \quad (12)$$

Since, $d(x^n) = nx^{n-1}$, the above equation can be simplified to

$$f(x) = -\frac{bpa\exp\left(-\frac{x}{r}\right)\left(\left(bp\exp\left(-\frac{x}{r}\right)\right)^{t}+1\right)^{-\frac{t+1}{t}}}{r} \qquad (13)$$

Replacing the parameters: $x = E^*$, $p = p_s$, $r = RT$, and $a = q_{\mathrm{m}}$ the site energy distribution function following a Toth isotherm explained in eq (1) is given by:

$$f(E^*) = -\frac{bp_s q_m \exp\left(-\frac{E^*}{RT}\right)\left(\left(bp_s\exp\left(-\frac{E^*}{RT}\right)\right)^{t}+1\right)^{-\frac{t+1}{t}}}{RT} \qquad (14)$$

References

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