Supporting Information

Derivation of Equations 9 and 11 for the Predictions of Isosteric Heat from an Isotherm

Equations 9 and 11 were derived from equations 8 and 10, namely the Langmuir and Tóth isotherm equations, by applying equations 3, 4 and 7.

For equation 9, the derivation is as follows.

Firstly, the Langmuir isotherm is expressed as

$$n^s = \frac{n_m^s p}{b+p} \quad (8).$$

Looking at the form of equation 3, first we take the derivative of pressure as a function of coverage as

$$\left.\frac{dp}{dn^s}\right|_T = \frac{(b+p)^2}{n_m^s b} \quad (S.1)$$

and multiply it by the Langmuir isotherm for coverage divided by pressure to yield

$$\frac{n^s}{p}\left.\frac{dp}{dn^s}\right|_T = \frac{1}{p}\frac{n_m^s p}{b+p}\frac{(b+p)^2}{n_m^s b} = \frac{b+p}{b} = \frac{p}{b}+1 \quad (S.2).$$

Subtracting 1 from equation S.2 and comparing it with equation 3, we arrive at the Tóth's correction (ψ) to the Polanyi potential function that is consistent with the Langmuir isotherm, namely

$$\frac{n^s}{p}\left.\frac{dp}{dn^s}\right|_T - 1 = \psi = \frac{p}{b} \quad (S.3).$$

Inserting this into equation 4 gives the Tóth potential function ($\Delta\lambda$) or

$$\Delta\lambda = RT\ln\left(\frac{\psi p^{sat}}{p}\right) = RT\ln\left(\frac{p^{sat}}{b}\right) \quad (S.4),$$

which can then be used in equation 7 to get

$$q_{st} \approx RT\ln\left(\frac{p^{sat}}{b}\right) + \lambda_p + RT \quad (9).$$

Equation 9 encapsulates our method for predicting the isosteric heat of adsorption for gases on solid adsorbents when the isotherm can be described by the Langmuir model (equation 8).

Similarly for equation 11, the derivation is as follows.

Firstly the Tóth isotherm model is expressed as

$$n^s = \frac{n_\infty^s p}{\left(b + p^m\right)^{1/m}} \tag{10}$$

We begin by taking the derivative of pressure as a function of coverage

$$\left.\frac{dp}{dn^s}\right|_T = -\frac{\left(b/\left(\theta^{-m}-1\right)\right)^{1/m}}{n^s\left(\theta^{-m}-1\right)} \tag{S.5}$$

and multiplying it by the Tóth isotherm divided by pressure to yield

$$\left.\frac{n^s}{p}\frac{dp}{dn^s}\right|_T = -\frac{n^s}{\left(b/\left(\theta^{-m}-1\right)\right)^{1/m}}\frac{\left(b/\left(\theta^{-m}-1\right)\right)^{1/m}}{n^s\left(\theta^{-m}-1\right)} = -\frac{1}{\theta^{-m}-1} \tag{S.6}$$

In accordance with equation 3, the Tóth correction to the Polanyi potential then takes the following form

$$\left.\frac{n^s}{p}\frac{dp}{dn^s}\right|_T - 1 = \psi = -\frac{1}{\theta^{-m}-1} - 1 \tag{S.7}$$

From equation 4, the Tóth potential function ($\Delta\lambda$) is then expressed as

$$\Delta\lambda = RT\ln\left(\frac{\psi p^{sat}}{p}\right) = RT\ln\left\{\frac{-p^{sat}\left[1+1/\left(\theta^m-1\right)\right]}{\left[b/\left(\theta^{-m}-1\right)\right]^{1/m}}\right\} = RT\ln\left[\frac{p^{sat}}{b^{1/m}}\left(\frac{\theta^m}{1-\theta^m}\right)^{(m-1)/m}\right] \tag{S.8}$$

which, when inserted into equation 7 gives our function for predicting the isosteric heat of adsorption when the isotherm conforms to the Tóth model (equation 10) or

$$q_{st} \approx RT\ln\left[\frac{p^{sat}}{b^{1/m}}\left(\frac{\theta^m}{1-\theta^m}\right)^{(m-1)/m}\right] + \lambda_p + RT \tag{11}$$