II G - Algebra of the Inflection Point Method

Using the quantum mechanical calculation a simple formula may be obtained for the monolayer equivalence for a non-porous material. This utilizes the inflection point in the isotherm which is always present for a non-porous material. The technique also reveals whether a material is porous or non-porous.

1) The first question is where is the inflection point?

Using the χ equation, this is simple to calculate by taking the first and second derivative. Here the designations $P^* := P/P_{vap}$ and $n := n_{ads}$ or as a function **n** are used. The starting equation is then more conveniently written as:

$$\theta = -\mathbf{ln}\left(-\mathbf{ln}\left(P^*\right)\right) - \chi_c \tag{501}$$

and θ is written depending upon the function $\mathbf{n}(P^*)$:

$$\theta = \frac{\mathbf{n}\left(P^*\right)}{n_m} \tag{502}$$

Differentiating once, one obtains from **Eq. (501)**:

$$\frac{\partial \mathbf{n}}{\partial P^*} = \frac{-n_m}{P^* \mathbf{ln}\left(P^*\right)} \tag{503}$$

and differentiating twice:

$$\frac{\partial^2 \mathbf{n}}{\partial P^*} = n_m \left(\frac{1}{\left[\mathbf{ln}\left(P^*\right)\right]^2} + \frac{1}{\mathbf{ln}\left(P^*\right)} \right) \tag{504}$$

Setting this second derivative to zero to find the inflection point pressure designated, P_I^* yields:

$$\frac{\partial^2 \theta}{\partial P^*} = 0 \Rightarrow \mathbf{ln}\left(P_I^*\right) = -1 \tag{505}$$

so that for the inflection point:

$$P_I^* = \mathbf{exp}\left(-1\right) \equiv \mathrm{e}^{-1} \cong 0.3678... \quad \Rightarrow \quad \mathbf{ln}\left(P_I^*\right) = -1 \quad \& \quad P_I^* \, \mathbf{ln}\left(P_I^*\right) \equiv -\mathrm{e}^{-1} \tag{506}$$

2) The next question is why one would want to know the inflection point?

The inflection point information can yield the monolayer equivalence and the value for χ_c or the energy of adsorption of the first adsorbate molecule. This is found by the following:

Substituting into **Eq. (503)** the slope at the inflection point is:

$$\frac{\partial \mathbf{n}\left(P_I^*\right)}{\partial P^*} = n_m \mathrm{e} \tag{507}$$

to find the tangent line to the inflection point, the intercept b in the equation is calculated at the inflection point:

$$\mathbf{n}\left(P^*\right) = n_m \mathrm{e} P^* + b \quad \text{specifically} \Rightarrow \quad b = \mathbf{n}\left(P_I^*\right) - n_m \mathrm{e} P_I^* \tag{508}$$

so:

$$\mathbf{n}\left(P^*\right) = n_m \mathrm{e} P^* + \mathbf{n}\left(P_I^*\right) - n_m \mathrm{e} P_I^* \tag{509}$$

but also from **Eq. (501)**:

$$\mathbf{n}\left(P_I^*\right) = n_m \left(-\mathbf{ln}\left[-\mathbf{ln}\left(P_I^*\right)\right] - \chi_c\right) \tag{510}$$

and substituting and evaluating **-ln**(P_I^*):

$$\mathbf{ln}\left(P_I^*\right) = n_m \left(-\mathbf{ln}\left[1\right] - \chi_c\right) \equiv -n_m \chi_c \tag{511}$$

thus:

$$b = n_{\mathrm{m}}\left(-\chi_{\mathrm{c}}\right) - n_m \mathrm{e} P_I^* \equiv n_{\mathrm{m}}\left(-\chi_{\mathrm{c}} - 1\right) \quad \mathbf{(512)}$$

and the final answer for the tangent is the line:

$$n = n_{\mathrm{m}}\left(P^* \mathrm{e} - \Delta\chi_{\mathrm{c}} - 1\right) \quad \mathbf{(513)}$$

(and at P_I^*:

$$n_I = n_{\mathrm{m}}\left(P_I^* \mathrm{e} - \Delta\chi_{\mathrm{c}} - 1\right) \qquad .) \quad \mathbf{(514)}$$

There are two potential questions that come up for this method:

1. Notice that the tangent line requires a value for $\Delta\chi_{\mathrm{c}}$. If this can not be determined then the value of n at P_I^* could be used to obtain the tangent line. However, in most cases one is not interested in this tangent line anyway. With good data, one could therefore determine the tangent line in this latter fashion and calculate $\Delta\chi_{\mathrm{c}}$ from **Eq. (512)** or **(513)**. So:

2. The second problem is if one were to attempt to determine where the inflection point is from experimental data, this would be very difficult. In the range from about P^* of 0.2 to 0.6 there is nearly a straight line - actually within 2%. So, by inspection it is nearly impossible to find the inflection point. However, the point of inflection, P_I^*, at $P^* = \mathrm{e}^{-1}$ (= 0.3678...) and the monolayer equivalence can be calculate then from Eq. **(507)**.

Summary:

In the isotherm using the amount adsorbed in moles, n_{ads}, versus the relative pressure, P/P_{vap}:

1. the inflection point for the curve, P_I^*, is at P/P_{vap}=0.3768... (e^{-1}).
2. The slope of the isotherm at this point, P_I^*, is equal to $\mathrm{e}n_{\mathrm{m}}$, (2.718... times the monolayer equivalence.)
3. If the $\Delta\chi_{\mathrm{c}}$ or E_{a} (recall the E_{a} definition - it is not a function of n_{ads}) is required then one can obtain this from the above equations or by reworking using:

$$\Delta\chi_{\mathrm{c}} = P_I^* \mathrm{e} - 1 - \frac{n_I}{n_{\mathrm{m}}} \quad \mathbf{(515)}$$

where n_I is the number of moles adsorbed at P_I^*.