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AN ADSORPTION EQUILIBRIA MODEL FOR STEADY STATE ANALYSIS

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ABSTRACT

The investigation of adsorption isotherms is a prime factor in the ongoing development of adsorption cycles for a spectrum of advanced, thermally-driven engineering applications, including refrigeration, natural gas storage, and desalination processes. In this work, a novel semi-empirical mathematical model has been derived that significantly enhances the prediction of the steady state uptake in adsorbent surfaces. This model, a combination of classical Langmuir and a novel modern adsorption isotherm equation, allows for a higher degree of regression of both energetically homogenous and heterogeneous adsorbent surfaces compared to several isolated classical and modern isotherm models, and has the ability to regress isotherms for all six types under the IUPAC classification. Using a unified thermodynamic framework, a single asymmetrical energy distribution function (EDF) has also been proposed that directly relates the mathematical model to the adsorption isotherm types. This fits well with the statistical rate theory approach and offers mechanistic insights into adsorption isotherms.

Keywords: Adsorption; Energy distribution function; Statistical rate theory; Universal isotherm model

1. INTRODUCTION

Several models have been used in the past to describe adsorbent and adsorbate systems under steady state conditions. These models have been useful in understanding the performance of assorted materials and vapor pairs under various conditions. Thermodynamic quantities, including enthalpy, entropy, and the specific heat capacity of the adsorbed phase, could be derived from the equilibria model. In this way, efficiencies such as the coefficient of performance (COP) and specific cooling effect (SCE) could be quantified. An adsorption equilibria model therefore allows for a comparative assessment of applications including adsorption cooling, desalination, and de-humidification processes.

2. THEORETICAL BACKGROUND OF ISOTHERM MODEL

By utilizing the concept of the gas phase chemical potential (Wedler & Borgmann, 1971; Jaroniec, 1983) and ideal gas assumptions, the equilibria-vapour uptake at assorted pressures and temperatures can be captured and expressed as:

$$\frac{q^*}{q_0} = \frac{0.5K_1\exp\left(\frac{P}{P_S}\right)\frac{P}{P_S}}{\left\{1+K_1\exp\left(\frac{P}{P_S}\right)\frac{P}{P_S}\right\}} + \frac{0.5AK_2\exp\left(\beta\frac{P}{P_S}\right)\frac{P}{P_S}}{\left\{1+K_2\exp\left(\beta\frac{P}{P_S}\right)\frac{P}{P_S}\right\}^t} \tag{1}$$

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where q^* represents the equilibrium uptake at temperature T and pressure P; q_0 is the limiting uptake at saturation pressure P_S; t is the surface heterogeneity factor; and K_1 and K_2 are the regression constants. The term β characterizes the energy of the adsorbent-adsorbate pair E_c and is related to the adsorption site energy of the adsorbent. A is a value calculated to ensure thermodynamic consistency of the model. The terms A and β can be expressed mathematically as:

$$A = \frac{[1 + K_2 \exp(\beta)]^t}{K_2 \exp(\beta)} \tag{2}$$

$$\beta = \exp\left(\frac{E_c}{RT}\right) \tag{3}$$

The proposed model satisfies the adsorption thermodynamic limiting conditions, so that:

(i) At zero pressure $\left(\lim_{P\to 0} \frac{q^*}{q_0} = 0\right)$, the proposed model shows null adsorbate uptake.

(ii) At pressure close to saturation $\left(\lim_{P\to P_S} \frac{q^*}{q_0} \approx 1\right)$, the adsorption equilibrium uptake of the proposed model approximately reaches the limiting uptake.

(iii) At pressure far lower than saturation pressure P_s, $\exp\left(\beta \frac{P}{P_S}\right) \approx 1$ and $\exp\left(\frac{P}{P_S}\right) \approx 1$, the proposed isotherm model reduces to Henry's linear relation where $\frac{q^*}{q_0} = 0.5(K_1 + AK_2)\frac{P}{P_S}$.

The proposed model is integrally a superposition of two parts. The first term on the right hand side is derived by modifying the classical Langmuir isotherm model and is used to describe the homogenous adsorbate uptake on the surface of the adsorbent. The second term on the right hand side, meanwhile, is a novel modern adsorption equation that introduces a heterogeneity factor, t, and is used to model the non-homogenous adsorbate on the surface of the adsorbent.

2.1. Regression of IUPAC Isotherms using Proposed Isotherm Model

Using only the calculation of the four regression parameters, E_c, t, K1, and K2, the proposed isotherm is able to regress all six types of IUPAC adsorbent-adsorbate pairs. Examples of such regressions, and their corresponding values, are presented in Figures 1-6 and Table 1, respectively.

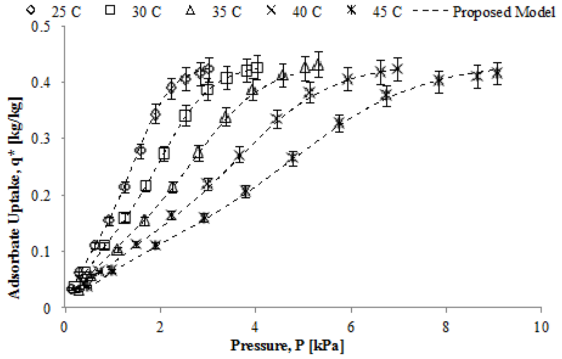

Figure 1 Regression of Type I silica gel 3A-water pair (Ang, 2014)

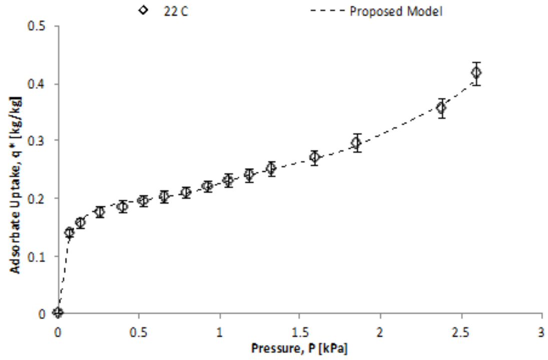

Figure 2 Regression of Type II poorly crystalline boehmite-water pair (Wang et al., 2003)

From the results, it is shown that the proposed model is able to accurately capture all the uptake shapes (convex, concave, S-shape, and others) of all IUPAC types of adsorbent-adsorbate pairs over a wide temperature range and for the full pressure range of adsorption, from vacuum to saturation pressure. As the regression parameters of the proposed model are dependent solely on the characteristics of the adsorbent-adsorbate pair, the model is able to regress the pair's isotherms at several temperatures over a wide range and can also be used to predict isotherms outside of this range using only a single set of regression parameters, as illustrated in Figures 1, 3, and 5.

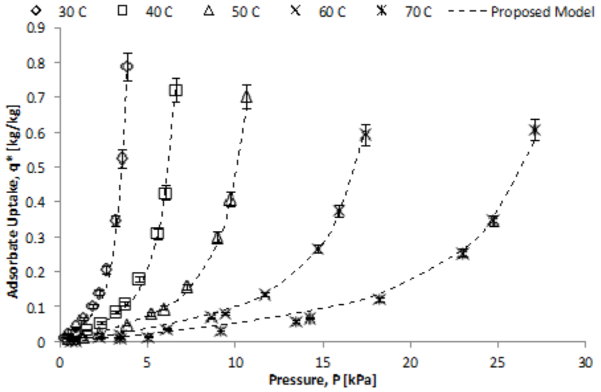

Figure 3 Regression of Type III green coconut pulp-water pair (Lavoyer et al., 2013)

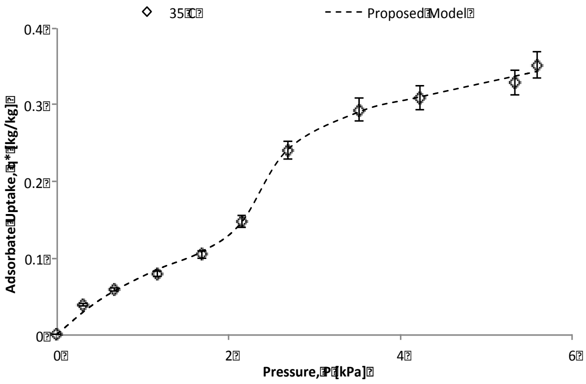

Figure 4 Regression of Type IV activated carbon PVDC600-water pair (Bansal & Dhami, 1978)

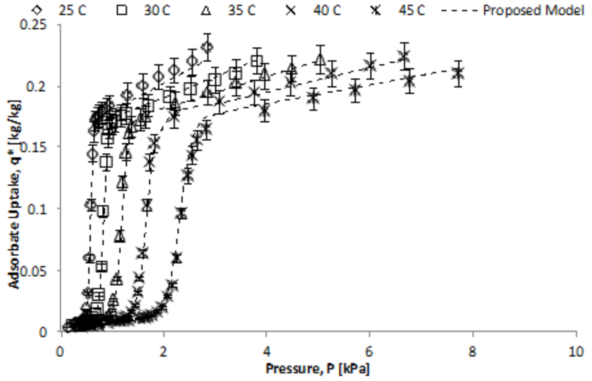

Figure 5 Regression of Type V zeolite FAM Z01-water pair (Ang, 2014)

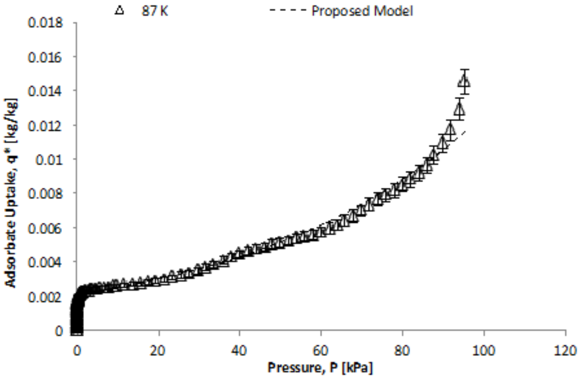

Figure 6 Regression of Type VI graphitized carbon black-argon pair (Gardner et al., 2001)

Table 1 Regression values of the isotherms illustrated in Figure 1

Regression value	Type I	Type II	Type III	Type IV	Type V	Type VI
*R^2	0.999^	0.997	0.995^	0.998	0.995^	0.986
**Error (%)	1.62^	2.23	8.36^	2.92	4.48^	18.1

* Coefficient of determination
** Normalized root mean square error to the mean experimental data
^ Regression values calculated are multiple isotherms of the working pair

2.2. Proposed Universal Energy Distribution Function (EDF)

From the "fundamental rate of gas molecule filling of adsorption from statistical rate" theory by Ward and colleagues (Elliott & Ward, 1997a; Elliott & Ward, 1997b; Ward et al., 1982; Elliott & Ward, 1997c), which was further developed by Rudzinski and colleagues (Rudzinski et al., 1999; Rudzinski et al., 2000; Rudzinski et al., 2001; Rudzinski & Panczyk, 2000), we have:

$$\frac{d\theta}{dt} = K'\left[\exp\left(\frac{\mu_g - \mu_\alpha}{RT}\right) - \exp\left(\frac{\mu_\alpha - \mu_g}{RT}\right)\right] \tag{4}$$

where θ is the proportion of the surface coverage equivalent to q^*/q_0; K' is the pre-exponential constant; and μ_g and μ_α are the chemical potential of the gaseous and adsorbed phases. Derived from this, the classical Langmuir (Rudzinski et al., 2001) isotherm model can be obtained for adsorption on energetically homogeneous surfaces and expressed as:

$$\theta = \frac{K\, exp\left(\frac{\varepsilon}{RT}\right)P}{1 + \, exp\left(\frac{\varepsilon}{RT}\right)P} \tag{5}$$

where ε is the activation energy of the homogeneous sites and K is the exponential constant.

However, when considering geometrical roughness and heterogeneity of a real adsorbent, uneven energy distribution of the surface should be considered. This is expressed by assuming that the surface can be divided into many infinitesimal pieces, each containing an average local adsorption site energy level that when combined, give the overall energy distribution of the surface. This can be expressed mathematically as:

$$\theta = \sum_i \chi(\varepsilon_i)\cdot\theta(\varepsilon_i) = \int_0^\infty \chi(\varepsilon)\cdot\theta(\varepsilon)d\varepsilon \tag{6}$$

where θ(ε) represents the local surface coverage and χ(ε) corresponds to the energy distribution function (EDF) of all adsorption sites of an energetically heterogeneous surface. The total EDF, when integrated across all energy levels, would produce unity as follows:

$$\int_0^\infty \chi(\varepsilon)\,d\varepsilon = 1 \tag{7}$$

Referencing the previously published concept of condensation approximation for moderate temperatures, the local surface coverage can be assumed to have a step-like behaviour, so that:

$$\begin{aligned}\theta &= \int_0^{\varepsilon_C} 0\cdot\chi(\varepsilon)\,d\varepsilon + \int_{\varepsilon_C}^\infty 1\cdot\chi(\varepsilon)\,d\varepsilon \\ &= \int_{\varepsilon_C}^\infty \chi(\varepsilon)\,d\varepsilon\end{aligned} \tag{8}$$

where the adsorption uptake function, θ, has two regions; one region of null uptake where the energy level is below the threshold activation energy level ε_c, and another region that is above the energy threshold activation energy level. ε_c can be expressed mathematically (Ismail et al., 2013) as:

$$\varepsilon_c = -RT\ln(K_2P) \tag{9}$$

Guided by the available EDF, χ(ε), of other empirical models such as Langmuir, Langmuir-Freundlich, Dubinin-Astakhov, Dubinin-Radushkevich, and Tóth (Rudzinski et al., 1999; Rudzinski et al., 2000; Rudzinski et al., 2001; Rudzinski and Panczyk, 2000), and using the statistical rate theory of adsorption framework, a single energy distribution function is proposed that relates the EDF directly to its isotherm types. The EDF, as expressed in Equation 10 below, incorporates an asymmetrical energy distribution and provides a theoretical basis for the proposed advanced universal adsorption isotherm model:

$$\chi(\varepsilon) = \frac{-0.5\beta^*}{RT}[\beta^* + \beta]\left[\frac{K_1 \exp\left(\frac{\beta^*}{\beta}\right)}{\left(K_1 \beta \exp\left(\frac{\beta^*}{\beta}\right) + \beta\right)^2}\right] + \frac{0.5AK_2}{RT}\exp(\beta^*)\frac{\beta^*}{\beta}(\beta^* + 1)\frac{\left[(1-t)K_2 \exp(\beta^*)\frac{\beta^*}{\beta} + 1\right]}{\left[1 + K_2 \exp(\beta^*)\frac{\beta^*}{\beta}\right]^{t+1}} \tag{10}$$

where the variable β^* is a function of the adsorption site energy, ε, and can be expressed as:

$$\beta^* = \exp\left(\frac{2E_c - \varepsilon}{RT}\right) \tag{11}$$

With the integration of the EDF of the proposed universal adsorption isotherm model, as shown in Equation 10, and with the substitution of Equation 9 as well as the expression E_c as shown in Equation 12, Equation 1 can be derived as:

$$E_c = -RT\ln(KP_s) \tag{12}$$

3. ADSORPTION ENERGY DISTRIBUTION PROFILE OF IUPAC ISOTHERMS

The adsorption energy distribution profile of the proposed EFD is for the six IUPAC types of isotherms (Figure 1) that are illustrated in Figures 7-12. From Figure 2, it is observed that the six IUPAC types of isotherms have different adsorption energy distributions, with certain adsorbent-adsorbate pairs displaying a profile with only a single peak while others display multiple peaks. This is due to the differing heterogeneity factor of an adsorbent-adsorbate pair, whereby surfaces that display a higher degree of heterogeneity are more likely to display multiple peaks in their adsorption energy distributions. With respect to the individual types of adsorbent-adsorbate pairs, the adsorption energy distributions alter with temperature. This is due to the temperature-dependent changes in the energies of the adsorbent and adsorbate at molecular level that influence the interaction between the solid surface and the adsorbate and adsorbent surfaces.

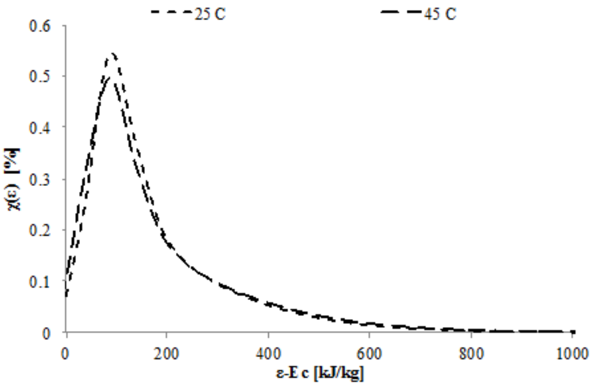

Figure 7 Energy distribution profile of Type I silica gel 3A-water pair

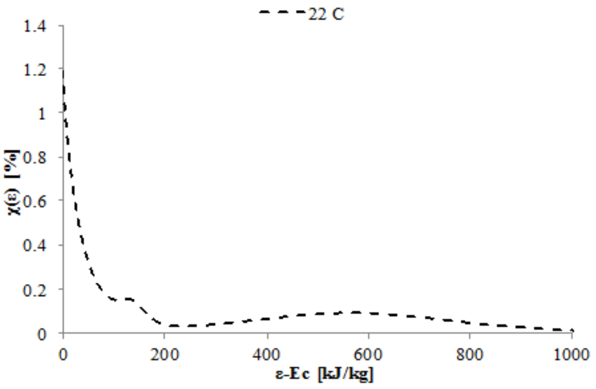

Figure 8 Energy distribution profile of Type II poorly crystalline boehmite-water pair

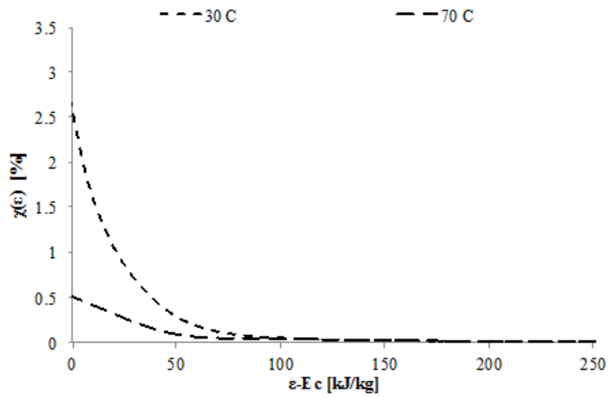

Figure 9 Energy distribution profile of Type III green coconut pulp-water pair

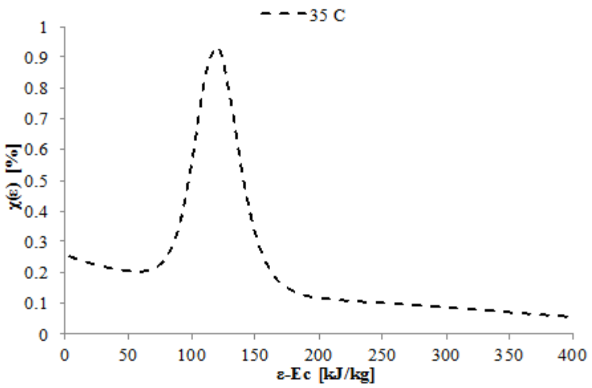

Figure 10 Energy distribution profile of Type II poorly crystalline boehmite-water pair

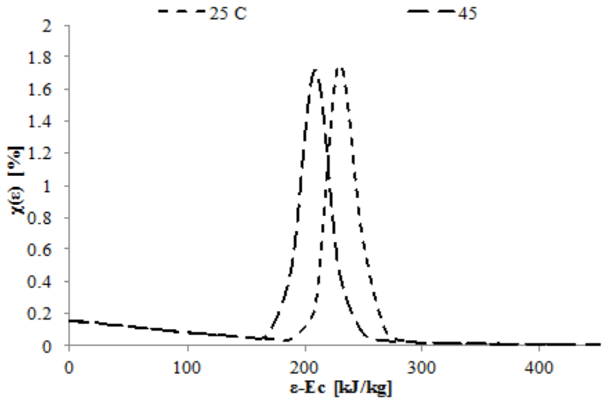

Figure 11 Energy distribution profile of Type IV activated carbon PVDC600-water pair

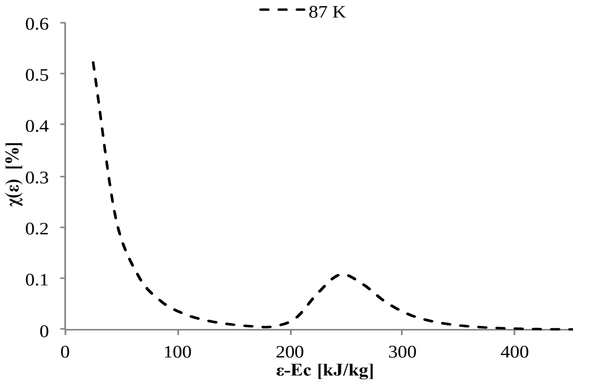

Figure 12 Energy distribution profile of Type VI graphitized carbon black-argon pair

4. CONCLUSION

An advanced universal isotherm model, which allows for a higher degree of regression of all six types of IUPAC isotherms, was presented in this work. Using statistical rate theory approach, a single asymmetrical distribution function of the adsorbent-adsorbate pairs was also proposed that exhibits single and multiple peaks in accordance with the adsorption energy distribution of the working pair. This relationship, along with others established in this work, provides a better understanding of the unified theoretical link between the various types of adsorbent-adsorbate statistical rate theory characteristics and the observed macro-scale adsorption phenomena.

5. ACKNOWLEDGEMENT

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