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Microporous and heterogeneous surface adsorption isotherms arising from Levy distributions

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Abstract

We show that for adsorption on heterogeneous and microporous surfaces, the Freundlich isotherm power-law exponent α is directly related to the Levy tail index of the distribution of the Langmuir parameter b and to the expected value and the variance of the adsorption energy distribution. This allows us to view adsorption at low pressure in these systems as a rare event dominated phenomena. Based on this discussion, a generalized isotherm formulation is proposed and applied to the interpretation of recent data on activated carbons.

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1. Generalized Langmuir isotherms

Adsorption isotherms represent the experimental measurements of the amount of materials adsorbed on surfaces as a function of pressure and temperature. Their shape depends on the nature of the gas, the nature of the surface, the nature of the interactions and the details of the surface coverage. Most isotherms used to fit experimental data are based on relatively simple thermo-statistical modes that are used outside the range of the hypothesis used to derive them. The most classical example is the BET method derived for multilayer adsorption [1]. For low pressure and low coverage the oldest and still commonly used isotherm formula is the so-called Langmuir equation which expresses the equilibrium between adsorption and desorption at a given T and macroscopic pressure for a monolayer

$$\theta(P) = \frac{b(E,T)P}{1 + b(E,T)P} . \tag{1}$$

The quantity θ represents the relative surface coverage or more generally the adsorbed quantity. The applied pressure P is generally expressed in units of the saturation vapor pressure P_0. The Langmuir factor is defined as

$$b = \kappa(T)\exp(E/kT) . \tag{2}$$

The quantity $K(T)$ is a statistical factor depending on the adsorption kinetics and the ratio of the partition function of the molecules in the adsorbed and gaseous state, respectively. E is the adsorption energy defined as the energy required to transfer a molecule from the lowest adsorbed state to the lowest gaseous state and resulting from all interactions giving rise to the resulting adsorption. The same formalism has been used for the adsorption of dissolved molecules in liquid solutions or soils. In that case θ is replaced by the concentration of chemical adsorbed (mg/kg) and P is the concentration remaining in solution (mg/1). For small pressure $P \ll b^{-1}$, the Langmuir isotherm reduces to the Henry isotherm (HI)

$$\theta(P) = bP .$$

The Langmuir isotherm (LI) considered as an empirical law has been useful to describe monolayer adsorption even when the Langmuir hypothesis, i.e., adsorption of non-interacting particles on a homogeneous "perfect" surface are not fulfilled. However, for heterogeneous and porous surface some other formulas had to be used to fit experimental data. The simplest generalization of LI is an extension of the HI known as the Freundlich isotherm (FI):

$$\theta(P) = K_F P^{\alpha} , \tag{3}$$

where α is a real number <1. The empirical generalized Langmuir isotherm (GLI) was introduced by Marczewski and Jaroniec in 1983 [6]

$$\theta(P) = \left(\frac{KP^n}{1 + KP^n}\right)^{m/n} . \tag{4}$$

According to the values given to the exponents $0 < m,\ n < 1$, one can recover other empirical power laws proposed in the literature: the LI for $(m = n = 1)$, the

Langmuir–Freundlich (LFI) for ($m = n < 1$), the Sips or General Freundlich (GFI) for ($n = 1, 0 < m < 1$) and the Toth (TI) for ($m = 1, 0 < n < 1$). The use of these empirical laws is by justified the fact that many opposite factors play a role in adsorption phenomena depending on the nature of the surface or the type of porosity. The consensus is that heterogeneity of the surface and pore size distribution on one hand and the influence of lateral molecular interactions on the other hand counterbalance each other. This can explain the quite universal successful use of these empirical formulas.

Nevertheless, since the paper of Zeldowitsch in 1934 [2], a number of works have been published in order to give more physical ground to the empirical isotherms and in particular the exponent in the FI. One way to achieve this objective has been to assume a distribution of local isotherms averaged with a distribution of local adsorption energies

$$\theta(P) = \int \frac{b(E,T)P}{1 + b(E,T)P} g_E(E)\,\mathrm{d}E \tag{5}$$

or

$$\theta(P) = \int \tilde{\theta}_{loc}(P) g_b(b)\,\mathrm{d}b \quad \text{with } \tilde{\theta}_{loc}(P) = \frac{b(E,T)P}{1 + b(E,T)P} \;.$$

This method is analogous to the so-called homottatic patch approximation in heterogeneous catalysis [7].

2. Generalized isotherms and Lévy distributions

In this paper, we want to reconsider this problem from quite a general perspective and to view the isotherm as a "*bona fide*" cumulative probability distribution, justify mathematically the existence of a power law and give a physical signification to the exponent α. As in many complex systems the occurrence of power laws is an indication of a heavy-tailed distribution for one or several variables of the problems. These distributions are now widely used in quite different statistical problems (dielectric and mechanical properties of heterogeneous materials, economics, queuing processes, traffic problems, etc.) and in many cases can be directly related to Levy stable distributions (LD).

As a pedagogical way to introduce this idea we will assume that the adsorption energy is distributed according to the distribution

$$g_E(E) \propto \exp(-E/E_0)\,, \tag{6}$$

where E_0 is a reference energy. This means that E has an exponential small probability to be large. This distribution has been proposed by a number of authors and since the works of Halsey [4] has been viewed as the origin of the power law behavior of isotherms at low pressure. The distribution of the parameter b in the LI can be obtained from Eqs. (2) and (6) using the probability theory property

$$|g_E(E)|\,\mathrm{d}E = |g_b(b)|\,\mathrm{d}b\,. \tag{7}$$

It is straightforward to show that b is a "α" variable [5] i.e.,

$$f(b) \propto kTb^{(-1-\alpha)} \quad \text{with } \alpha = \frac{kT}{E_0} \, . \tag{8}$$

This result means that the variable b in this particular example has a probability distribution which belongs to a distribution characterized by the tail index α. It is of interest to note that if α is smaller than 1, b is a statistical variable whose distribution has infinite moments. An expression has been coined by Boucheau [5] to describe this situation peculiar to heterogeneous materials such as glasses. It is referred to as the "*exponential conspiracy*". The consequences of this mathematical property will be further investigated.

If we use this distribution we can write

$$\theta(P) = \int_1^{\infty} \frac{bP}{(1+bP)} g_b(b)\,\mathrm{d}b \quad \text{with } g_b(b) = \frac{b^{(-1-\alpha)}}{\int_1^{\infty} b^{(-1-\alpha)}\,\mathrm{d}b} = \alpha b^{-1-\alpha} \, . \tag{9}$$

The function $g_b(b)$ is the Pareto probability density distribution defined for $b > 1$. If $\alpha < 1$, the expectation value $E(b) = \infty$ and $g_b(b)$ belongs to the domain of attraction of the one-sided stable-Lévy distributions. The integrand is a product of a cumulative (cdf) and a density probability distribution (pdf). As a consequence $\theta(P)$ has the form of a cdf.

After integration, using the properties of hypergeometric functions $F[a, b, c; z]$ we obtain the following simple compact result:

$$\theta(P) = \left(\frac{P}{P+1}\right)^{\alpha} F\left[\alpha, \alpha, 1+\alpha, \frac{1}{P+1}\right] . \tag{10}$$

Since

$$F[\alpha, \alpha, 1+\alpha, 1] = \pi\alpha csc[\pi\alpha] \tag{11}$$

we have

$$\theta(P, \alpha) \to KP^{\alpha} \quad \text{for } P \to 0 \quad \text{with } K = \pi\alpha csc[\pi\alpha] \, . \tag{12}$$

If $\alpha < 1$, the hypergeometric function can be written as an absolute convergent Gauss hypergeometric series, we can write:

$$\theta(P) = \frac{\alpha}{\Gamma(\alpha)} \left(\frac{P}{P+1}\right)^{\alpha} \sum_{n=0}^{\infty} \frac{1}{n!} \frac{\Gamma(\alpha+n)}{\alpha+n} (P+1)^{-n} \, . \tag{13}$$

For $\alpha = 1$ and $\alpha = 0.5$, one can obtain analytic solutions

$$\theta(P) = P \ln \frac{P+1}{P} \quad \text{for } \alpha = 1 \, , \tag{14}$$

$$\theta(P) = P^{1/2} \arcsin\left(\sqrt{\frac{1}{P+1}}\right) \quad \text{for } \alpha = 0.5 \, . \tag{15}$$

In many results discussed in the literature, the bounds are taken from 0 to ∞ for mathematical convenience. It has to be noted that here we have chosen the correct limit since, adsorption energies have to be positive and, therefore, solution (13) is the exact isotherm for the adsorption energy distribution (6). In these isotherms the T dependence of θ is given by the variation of α with T which, as we will see, is linear. In the theoretical discussions isotherms correspond to a micropore volume equal to unity and we will use K_α and P is the relative pressure of the adsorbate.

As the isotherm has the form of a cumulative distribution function, we can write formally

$$\theta(P) = \int_0^P f_\theta(p)\,\mathrm{d}p \quad \text{with}\, f_\theta(p) = \frac{\partial\theta(p)}{\partial p}\,. \tag{16}$$

For the FI $\theta(P) = K_\alpha P^\alpha$, we have $= K_\alpha \alpha p^{\alpha-1}$. The local random variable p which is related to the random variable E by

$$p_i = \exp(-E_i/kT) \tag{17}$$

has to be understood in the following way: the first molecules to arrive at the surface are adsorbed preferentially on the most attractive sites which belong to the tail of the distribution of E. As these sites become filled the less actives sites become filled and adsorption takes place on sites of progressively decreasing activity. To each local value E_i we can associate the local pressure value p_i given by Eq. (17), which is the random variable of the distribution function $f_\theta(p)$. This observation is consistent with the fact that the distribution $g_b(b)$ belongs to the domain of attraction of the one-sided stable-Lévy distributions. The adsorption phenomena can, therefore, be viewed as a phenomenon dominated by rare events, i.e., the adsorption sites of very large values of b and consequently of large values of E and small values of p. This quantitative discussion should be pursued using more elaborate probability theory arguments. If the expectation value of b is infinite, the average value of E can be defined properly and, as we will show in the next section, is directly related to the experimental macroscopic quantity α, the heavy tail index of the distribution of the GLI parameter b.

3. Physical interpretation of exponent α

The adsorption energy pdf corresponding to the Pareto distribution (9) can be written using (2)

$$g_{E,\alpha}(E) = (\alpha/kT)\exp[-\alpha(E/kT)] \tag{18}$$

from which one can calculate the finite expectation value and variance of the adsorption energy distribution.

$$\langle E\rangle = \frac{kT}{\alpha} \quad Var(E) = \sigma^2 = \langle E^2\rangle - \langle E\rangle^2 = \left(\frac{kT}{\alpha}\right)^2\,. \tag{19}$$

This result provides a simple physical interpretation of the reference energy E_0 which here is the average adsorption energy $\langle E\rangle$. The exponent α is a measure of the energy average and the width of the adsorption energy distribution, both increase when α

decreases. In the adsorption literature the function $g_{E,\alpha}(E)$ is known as the Zeldovich–Roginsky formula and it corresponds to a canonical distribution "frozen" at a temperature $T^* = T/\alpha > T$, where T is the current temperature of the system. According to this point of view, the characteristic temperature T^* should give some indication on the surface processing. As mentioned earlier, although the expectation of the random variable b is infinite if $\alpha < 1$, the expectation value of the random adsorption energy is finite since $g_{E,\alpha}(E)$ belongs to the domain of attraction of the normal distribution.

The distribution $g_b(b)$ cannot be reduced to its heavy tail asymptotic behavior and it can be assumed that the real distribution function belongs to the basin of attraction of one-sided Lévy distributions. The LD does not have an analytical form; however it is known [16] that its asymptotic expression

$$Fr(x,\alpha) = \alpha \exp(-x^{-\alpha})x^{-\alpha-1} \tag{20}$$

can be used to approximate it for $\alpha < 1$ and $x > 1$. This function is known in probability theory as the Fréchet distribution. If we use this density distribution as the distribution of the Langmuir parameter b, we have

$$\theta(P) = \int_1^\infty \frac{bP}{1+bP}\, g(b)\,\mathrm{d}b \quad \text{with } g_b(b) = \frac{Fr(b,\alpha)}{\int_1^\infty Fr(b,\alpha)\,\mathrm{d}b} \tag{21}$$

and expanding the exponential in Eq. (20), we obtain the solution

$$\theta_{Fr}(P) = \sum_{m=0}^{\infty} \frac{(-1)^m}{(m+1)!}\left(\frac{P}{P+1}\right)^{\alpha(m+1)} \times F\left[(m+1)\alpha, (m+1)\alpha, 1+(m+1)\alpha, \frac{1}{P+1}\right]. \tag{22}$$

It has been demonstrated that the Frechet distribution maximizes the Shannon–-Boltzmann entropy if we impose constraints on $\int \ln xf(x)\,\mathrm{d}x$ and $\int x^{-\alpha}f(x)\,\mathrm{d}x$ [8]. In this context this means constraints on $\langle E\rangle$ and $\langle \exp[-\alpha(E/kT)]\rangle$.

Using the Fréchet distribution for variable b, one finds easily that

$$\int_0^\infty \frac{E}{kT}\, g_F(E) = c_E\,\frac{1}{\alpha} \to \alpha = \frac{1}{c_{\langle E\rangle}}\,\frac{kT}{\langle E\rangle} \tag{23}$$

with

$$g_F(E) = c_E \alpha \mathrm{e}^{[-\alpha E/kT]}\mathrm{e}^{[-\mathrm{e}^{(-\alpha E/kT)}]} \tag{24}$$

a function which is known as the extreme value distribution. Using this distribution we find

$$\langle E\rangle = c_{\langle E\rangle}\,\frac{kT}{\alpha}\,, \tag{25}$$

$$Var(E) = \sigma_E^2 = \langle E^2\rangle - \langle E\rangle^2 = c_\sigma\left(\frac{kT}{\alpha}\right)^2. \tag{26}$$

The constants c_E, $c_{\langle E\rangle}$ and c_σ are of order 1. These results obtained with a more realistic adsorption energy distribution confirms the one (19) obtained with the Pareto distribution, i.e., the exponent α is a direct measure of the standard deviation σ of the distribution and the average of the site adsorption energy. The larger α, the smaller σ_E and $\langle E\rangle$.

4. Relation of Freundlich exponent α with the non-extensive entropic q index

Classical thermodynamics [3] does not provide isotherms with power-law behavior. It is, therefore, legitimate to ask the following question. Would non-extensive thermodynamics [12] lead to power-law isotherms and what could be the relation between the empirical exponent α and the non-extensive Tsallis q parameter. Our purpose here is to give a preliminary answer to that question. Interestingly, if we follow the conjecture proposed by Drazer and Zanette [9] that the local equilibrium constant $b(E,T)$ is proportional to the trapping time τ of a molecule on the surface $b = w\tau$, we have

$$\theta(P) = \int_0^\infty \tilde{\theta}_{loc}(\tau)\varphi(\tau)\,\mathrm{d}\tau = \int_0^\infty \frac{w\tau P}{1 + w\tau P}\,\varphi(\tau)\,\mathrm{d}\tau \,. \tag{27}$$

If we use $\varphi(\tau)$, the density function which maximizes the Tsallis entropy [12,14] for the random waiting time τ that has been used in the problem of dielectric relaxation [18]

$$\varphi(\tau) = \frac{1}{\langle\tau\rangle_q}\left(1 + \frac{q-1}{2-q}\,\frac{\tau}{\langle\tau\rangle_q}\right)^{-1/(1-q)}, \tag{28}$$

where q is the Tsallis entropy index characterizing the degree of non-extensivity $1<q<2$ and $\langle\tau\rangle_q$ is the escort distribution average [12]

$$\langle\tau\rangle_q = \frac{\int_0^\infty \tau\varphi(\tau)^q\,\mathrm{d}\tau}{\int_0^\infty \varphi(\tau)^q\,\mathrm{d}\tau} \,. \tag{29}$$

Geometrically, the use of Tsallis function can be justified by the work of Cordeiro and collaborators [19] which shows that the structure of irregular surfaces may be represented by distributions exhibiting heavy Levy–Tsallis tails. The function $\varphi(\tau)$ belongs to the domain of attraction of the one-sided stable Lévy distribution with tail index $\alpha = (2-q)/(q-1)$, which gives $q = (\alpha+2)/(\alpha+1)$. After integration and some calculations involving hypergeometric functions properties, it is easy to show that

$$\theta = K_\alpha P^\alpha \quad \text{for } P \ll 1 \,. \tag{30}$$

If we define the time unit as $\tilde{\tau} = (2-q)/(q-1)\langle\tau\rangle_q = 1$, the constant K_α is given by $\pi\alpha csc[\pi\alpha]$ the same coefficient as for the Pareto distribution (12). This reflects the fact that for small P, the behavior of the isotherm is dominated by the heavy tail behavior of the distribution of the random variable τ (or b). If $\alpha<1$, i.e., $\frac{3}{2}<q<2$, the usual expectation value $\langle \tau \rangle_{q=1}$ is infinite. The formalism based on the maximization of the Tsallis entropy provides a finite natural time scale and resolves some inconsistencies of the Drazer and Zanette model pointed out in Ref. [10]. Following the discussion in Ref. [18], the q non-extensive parameter and the heavy tail properties of the trapping-time distribution are directly related to the random number of adsorbing entities participating in the adsorption process at the meso- or microscopic level. This gives rise to fluctuations of the usual extensive (i.e., corresponding to exponential distribution) time scale. In the sense that Tsallis entropy can be viewed as a technique to define a finite scale when the number of entities participating to the spatiotemporal dynamic process is statistically fluctuating due to natural geometric constraints. This is the case for heterogeneous surfaces and porous materials. The scale can be defined as a q-expectation value using the concept of Tsallis entropy escort probability [18,12].

5. Weibull distribution as a possible empirical isotherm

Among the probability distributions $F(x)$ used in physics having the asymptotic property $F(x) \to x^{\alpha}$ for $x \to 0$, one of the most widely used is the Weibull distribution. We have made the following observation: numerically the isotherm $\theta(P, \alpha)$ is very close to the Weibull distribution for $P < 1$.

$$\theta_W(P) = 1 - \exp[-K_{\alpha} P^{\alpha}] . \tag{31}$$

In Fig. 1 we show the two quasi-indiscernible functions for $\alpha = 0.5$. The constant from Eq. (12) is $K_{\alpha}(\alpha = 0.5) = 0.5708$.

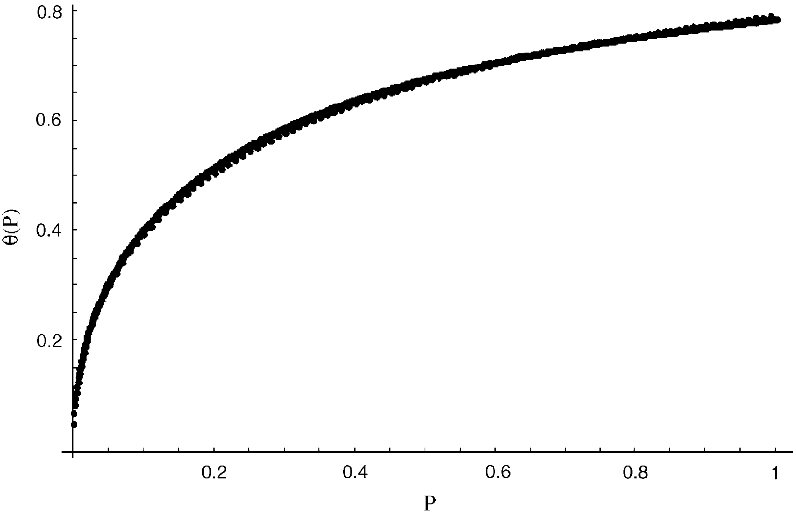

Fig. 1. GLI (Eq. 10) (full line) and Weibull isotherm (dotted line) for $\alpha = 0.5$.

This can be understood at least for $P \ll 1$ with the following argument. The relation between stretched exponential and LD is well known in the theory of relaxation [15,13]. The Laplace transform of one-sided LD is a stretched exponential whose stretching exponent $\alpha < 1$ is the heavy tail exponent of the one-sided LD. We can write the GI using a normalized one-sided LD $g_L(b)$ assuming that the integration runs from 0 to ∞ as this has been generally done in the literature. Since the integration is dominated by the tail of the distribution, we have

$$\theta(P) = \int_0^\infty \frac{bP}{1+bP}\, g_L(b)\,\mathrm{d}b = \left(1 - \int_0^\infty \left(\frac{1}{1+bP}\right) g_L(b)\,\mathrm{d}b\right) . \tag{32}$$

If we notice that the second term is the approximation for low p of the Laplace transform

$$\int_0^\infty \exp(-bP) g_L(b)\,\mathrm{d}b \tag{33}$$

one can infer immediately using the theorem relating to one-sided LD to stretched exponential [15] that the isotherm is a Weibull distribution with an exponent α,

$$\theta(P) = 1 - \exp(-K_\alpha P^\alpha) = \int_0^P f_\theta(p)\,\mathrm{d}p \tag{34}$$

and the corresponding pdf

$$f_\theta(p) = K_\alpha \exp[-K_\alpha p^\alpha] .$$

For very small P this isotherm reduces to the FI:

$$\theta(P) = K_\alpha P^\alpha . \tag{35}$$

More generally, and more convincingly, we can justify the use of the Weibull distribution as an empirical isotherm for heterogeneous surfaces by invoking once again the principle of maximum entropy and use the expression (17) for p and the Zeldovich–Roginsky distribution (18) for the adsorption energies E, we see immediately that the exponent α is simply related to the average of $\log p$:

$$\langle \log p \rangle = -1/\alpha . \tag{36}$$

For the Weibull distribution we have

$$\langle p^\alpha \rangle = K_\alpha^{-1} \quad \langle \log p \rangle = \frac{\ln K_\alpha - \gamma}{\alpha} , \tag{37}$$

where γ is the Euler constant. Interestingly, given the knowledge of the macroscopic observable α, the Weibull distribution is a distribution, which under the two constraints (36), (37) maximizes the Shannon–Boltzmann entropy [11,18]:

$$-\int f(p) \log f_\theta(p)\,\mathrm{d}p \quad \text{with } f_\theta(p) = \frac{\partial \theta(p)}{\partial p} . \tag{38}$$

The use of Weibull isotherms to fit data of a number of activated carbons for relative pressure corresponding to micropore adsorption indicates that the fitting procedure is much better than any other empirical formula. For $\alpha \preccurlyeq 0.2$, the Freundlich law which is the small α limit of the Weibull isotherm as well as of isotherm (13) is good. Analysis of experimental data using the FI and Weibull isotherms have been used quite successfully to analyze the adsorption data of a number of microporous activated carbon and zeolites and systematic correlations with the usual adsorption characteristic quantities have been found. The results will be presented elsewhere.

6. Analysis of isotherm data of activated carbons

We will give here one example based on the work of one of us [17] on powered activated carbons from *pinus caribaea* sawdust prepared with the use of CO_2 and steam as active agents. From the discussion of the data of this work, it appears (Tables 1 and 2) that for this type of materials, the experimental constant K_F is proportional to the BET surface area and the microporous volume while the exponent α varies linearly with absolute T and increases slightly with the burn-off values. These two quantities measure the change of adsorbing power and adsorption energy distribution resulting from the change of the microporous heterogeneity when temperature burn-off and activation energy are modified. The value of α increases with an increase in burn-off, i.e., with the widening of the micropore size distribution as described in Ref. [17]. The physical interpretation of this phenomenon [20,21] is that burn-off increase widens micropores, creates and opens more pores and as a consequence the average interaction energy between the porous system and the adsorbate gas molecules decreases as the pore mean diameter increases [Fig. 2].

7. Conclusions

Using arguments borrowed from the theory of stable Levy distributions and the principle of maximization of generalized entropy, we have given a physical interpretation of the empirical power-law Freundlich isotherm. This analysis indicates that the two parameters K_F and α can characterize the adsorption power and the active site distribution of the adsorbant–adsorbate system, and are the two relevant macroscopic observables, which can provide an isotherm function when

Table 1
Values of Freundlich law parameters, BET surface area and micropore volume of CO_2-activated carbons

Carbon	K_F	α	q	BET surface area m^2/g	V_{mic}	% burn off
C75029	209	0.075 ± 0.005	1.93	575	0.27	29
C75061	362	0.096	1.91	969	0.46	61
C75077	386	0.112 [Fig. 2]	1.89	1021	0.48	77
C87528	212	0.090	1.92	631	0.26	28
C87548	286	0.094	1.90	783	0.38	48

Table 2
Values of Freundlich law parameters, BET surface area and micropore volume of steam-activated carbons

Carbon	K_F	α	q	BET surface area m^2/g	V_{mic}	% burn off
S72527	211	0.12 ± 0.05	1.89 ± 0.1	570	0.28	27
S72547	247	0.13	1.88	732	0.31	47
S72561	342	0.14	1.87	895	0.37	61
S72571	402	0.15	1.86	1038	0.43	71
S85029	239	0.13	1.88	617	0.27	29
S85049	342	0.15	1.86	790	0.34	49
S85068	401	0.16	1.85	937	0.38	68
S85075	402	0.16	1.85	1034	0.39	76

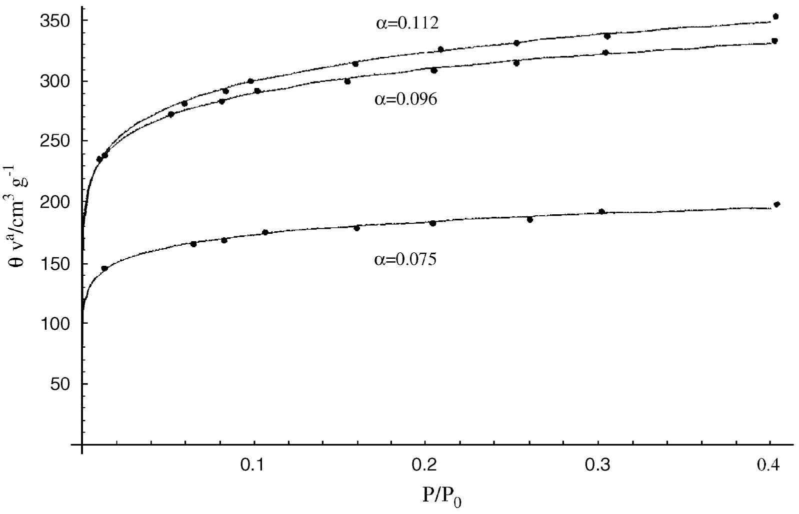

Fig. 2. Isotherm of activated carbon C750 (see Table 1).

maximizing the entropy of the local random pressure. This function is the Weibull distribution which for low applied pressure P tends to the Freundlich isotherm. This provides a new insight into the old problem of adsorption inheterogeneous systems.

References

[1] S.J. Gregg, K.S.W. Sing (Eds.), Adsorption, Surface Area and Porosity, second ed., Academic Press Inc., New York, 1982.
[2] J. Zeldowitsch, Acta Physicochim., URSS 1 (1934) 961.
[3] R.H. Fowler, Proc. Camb. Phil. Soc. 31 (1936) 260.
[4] G.D. Halsey Jr., H.S. Taylor, J. Chem. Phys. 15 (1947) 624.

[5] J.P. Boucheau, in: M.F. Shlesinger (Ed.), Levy Flights and Related Topics, Springer, Berlin, 1996, p. 239.

[6] W. Marczewski, M. Jaroniec, Mth. Chem. 114 (1983) 711.

[7] W. Rudzinski, H.D. Evrett, Adsorption of Gases on Heterogeneous Surfaces, Academic, London, 1992.

[8] Yu. Krawich, V. Mergel, in: 31st ASTIN Proceedings, Poste Corro, Sardinia, September 2000.

[9] G. Drazer, D.H. Zanette, Phys. Rev. E 60 (1999) 5868.

[10] M.O. Vlad, G. Ceropolini, J. Ross, Phys. Rev. E 62 (2000) 837.

[11] J.N. Kapur, Maximum Entropy Models in Science and Engineering, Wiley, New York, 1989.

[12] C. Tsallis, in: S. Abe, Y. Okamoto (Eds.), Non Extensive Statistical Mechanics and Thermodynamics, Springer, Berlin, 2001 and references therein.

[13] K. Weron, M. Kotulski, J. Stat. Phys. 88 (1997) 1241.

[14] F. Brouers, O. Sotolongo-Costa, Europhys. Lett. 62 (2003) 808.

[15] E.W. Montroll, J.T. Bendler, J. Stat. Phys. 34 (1984) 129.

[16] V.V. Uchaikin, V.M. Zolotare, Chance and Stability, VSP, Utrecht, 1999.

[17] F. Marquez-Montesimos, T. Cordero, J. Rodriguez-Mirasol, J.J. Rodriguez, Sep. Sci. Technol. 36 (2001) 3191.

[18] F. Brouers, O. Sotolongo, K. Weron, Physica A 344 (2004) 409.

[19] J.A. Cordeiro, M. Lima, VR. Dias, F. Oliveira, Physica A 295 (2001) 209.

[20] P. Lodewick, private communication.

[21] F. Stoeckli, Characterisation of microporous carbons by adsorption and immersion techniques, in: J.W. Patrick (Ed.), Porosity in Carbons, Edward Arnold, 1995, pp. 70–72.