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Dubinin´s theory and its contribution to adsorption science*

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Dubinin´s theory for the volume filling of micropores (TVFM), originally developed for the adsorption of single vapours by microporous solids such as activated carbons and zeolites, has gradually been extended to other areas. They include immersion calorimetry, the adsorption of water vapour and of mixtures, as well as adsorption from aqueous solutions. Recent studies in the field of adsorption from aqueous solutions, by activated carbons, suggest that the principle of temperature invariance is fulfilled and in the case of phenolic compounds a modified DRK equation can be used to predict the adsorption equilibrium over a certain range of temperatures. Computer modelling of CO_2 adsorption by carbons at 273 K leads to micropore distributions, which are in good agreement with those derived from other techniques. It also appears that the model isotherms in single slit-shaped micropores can be fitted to the Hill-de Boer isotherm, in agreement with mathematical studies of the origin of the Dubinin—Astakhov equation.

Key words: adsorption, microporosity, immersion calorimetry, activated carbons, simulation.

In 1947 the late Academician M. M. Dubinin (1901—1993) and his collaborators published the first paper[1] on adsorption by activated carbons and proposed the classical equation of Dubinin and Radushkevich. This novel approach was based on a concept developed by Polanyi[2] and it set the stage for the description of adsorption of vapours by carbons and other microporous adsorbents, known as Dubinin´s theory for the volume filling of micropores (TVFM).[3—12] It is interesting to point out that more than fifty years later, this theory still enjoys popularity among scientists and it has produced unexpected developments in the field of adsorption science. This success is mainly due to the fact that the theory is based on a thermodynamic potential, which provides a suitable framework for a rigorous treatment.

As shown in a collection of papers dedicated to the memory of M. M. Dubinin,[8] the possibilities offered by TVFM go beyond the original expectations of its author and the theory has been extended to other domains in adsorption science.[13] These include immersion calorimetry,[8,14] the adsorption of vapour mixtures[15,16] by activated carbons and zeolites, and adsorption from solution,[17] to quote the most important developments. It has also been shown, in collaboration with Dubinin´s laboratory,[14—18] that the adsorption of water by activated carbons can be described within the framework of Dubinin´s theory. It is a property of great technical and

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theoretical importance, which illustrates the potential of this approach.

In the present paper, we discuss recent developments of Dubinin′s theory, some of which were obtained by the present author and have not been published yet. A number of earlier contributions to surface science also resulted from a direct collaboration with M. M. Dubinin and later with members of his school.

The fundamentals of Dubinin′s theory

Following the generalization proposed in 1971,[3] the fundamental equation of TVFM is the so-called Dubinin—Astakhov equation (DA),

$$N_a = N_{a0}\exp[-(A/E)^n], \qquad (1)$$

where N_a represents the amount adsorbed at relative pressure p/p_s, N_{a0} is the limiting amount filling the micropores and $A = RT\ln(p_s/p)$. The latter is a thermodynamic potential and $A = -\Delta G_{ads}$, the reference being the saturated vapour at T and p_s. At high pressures, the ratio p_s/p is replaced by the ratio of the fugacities f_s/f and for temperatures above critical, the saturation pressure is replaced by an expression given by Dubinin and Nikolayev.[3] Since Eq. (1) reflects the filling of a volume, it is convenient to replace the limiting amount N_{a0} by the micropore volume $W_0 = N_{a0}V_m{}^a$, where $V_m{}^a$ is the molar volume in the adsorbed state at the given temperature. As a first, and usually good approximation, one may use the molar volume in the liquid state, but it appears that the two are not necessarily identical. For example, for CO_2 at 273 K one finds $V_m{}^a$ = 42.9 cm^3 mol^{-1}, against 48.2 cm^3 mol^{-1} in the liquid state. The difference is probably due to the packing of the molecules in the pores.

Exponent $n = 2$ corresponds to the classical Dubinin—Radushkevich equation (DR) and E is the so-called characteristic energy of the system. It depends on the adsorbent and on the adsorptive, but one may write that $E = \beta E_0$, where β is a coefficient depending only on the adsorptive. By convention, benzene is the reference and $\beta(C_6H_6) = 1$. Values of β have been tabulated[19] and relations have been proposed for their calculation.

At an early stage, the exclusion of larger molecules by certain carbons suggested that the so-called structural constant B (a quantity used prior to E_0), is related to the size of the micropores. Later, the small-angle scattering of X-rays[20] suggested that the gyration radius of the micropores is an inverse function of the characteristic energy. At the present time, a variety of independent techniques, including recent observations by STM[13] suggest the following empirical correlation between the average width L_0 (nm) of the micropores and E_0 (kJ mol^{-1}),

$$L_0 = 10.8/[E_0 - 11.4\ (\text{kJ mol}^{-1})] \quad (0.4\ \text{nm} < L_0 < 2\ \text{nm}). \qquad (2)$$

Table 1. Structural parameters of some well characterized porous carbons, derived from Eqs. (1)—(3) and from Monte Carlo simulations of CO_2 adsorption at 273 K

Carbon	W_0 /cm^3 g^{-1}	E_0 /kJ mol^{-1}	L_0/nm		S_e	$S_{mi}{}^a$	$S'_{mi}{}^b$
			I^c	II^b	m^2 g^{-1}		
CM	0.252	28.0	0.65	0.84	5	875	690
CAF-B	0.266	28.3	0.65	0.75	60	856	749
C-400	0.130	26.7	0.70	0.86	12	369	321
XC-72	0.057	22.4	0.96	1.01	105	145	140
XC-72-16	0.130	21.3	1.08	1.22	119	259	294
U-103	0.330	20.7	1.15	1.28	39	631	625
KF-1500	0.580	19.1	1.38	1.46	21	918	904

[a] Calculated using Eq. (3).
[b] Monte Carlo simulation.
[c] Calculated using Eq. (2).

The surface area of the locally slit-shaped and open micropores, S_{mi} (m^2 g^{-1}), corresponds approximately to

$$S_{mi} = 2000W_0\ (\text{cm}^3\ \text{g}^{-1})/L_0. \qquad (3)$$

In view of the simplicity of the parameters required by Dubinin′s theory (readily available physical properties such as p_s, V_m, and β), Eq. (1) allows the description of single vapour adsorption by microporous solids over a wide range of pressures and temperatures. Moreover, Eqs. (2) and (3) provide information on the structural properties of activated carbons and interesting correlations have recently been obtained by computer simulations based on Monte Carlo techniques.[21,22] As shown in Table 1, one observes a good agreement between the values of L_0 and S_{mi} obtained from Eqs. (2) and (3) and from the analysis based on computer simulations of CO_2 adsorption at 273 K.

The problem of heterogeneity of the micropore system in activated carbons has been examined jointly by Dubinin and Stoeckli.[4] This led eventually to the DS (Dubinin—Stoeckli) equation.[5,9] It is based on a Gaussian distribution of the micropore widths L, assuming the simple relation L (nm) = $26/E_0$ (kJ mol^{-1}). This distribution has been verified,[23] by comparing the predictions of the DS equation with direct observations by STM. It has also been shown[9] that reasonable pore size distributions can be derived from an alternative to Eq. (1),

$$\theta(A) = N_a/N_{a0} = \{a/[a + (A/\beta K_0)^3]\}^{\nu}. \qquad (4)$$

It results from an integral transform, involving a local DA equation with $n = 3$ and the micropore distribution

$$f(L) = 3W_0L^{(3\nu-1)}a^{\nu}\exp(-aL^3)/\Gamma(\nu). \qquad (5)$$

In these expressions, a and ν are adjustable parameters and K_0 is related to the average micropore width L_0 by $K_0 = L_0E_0$. As shown below, this approach leads to a good agreement with the pore size determinations based on immersion calorimetry with liquid probes of variable molecular dimensions, and on computer simulations.

Dubinin´s theory is not limited to the volume filling of micropores.[24] This author suggested that a modified form of Eq. (1), later called the Dubinin—Radushkevich—Kaganer (DRK) equation, could be used to describe adsorption on non-porous surfaces,

$$N_a = N_{am}\exp[-(A/E)^2], \quad (6)$$

The quantity N_{am} represents the monolayer capacity of the surface. Eq. (6) was presented as an alternative to the BET equation, which applies at higher relative pressures ($0.5 > p/p_s > 0.30$—0.35). However, its use was limited to a few adsorbates, mainly N_2 at 77 K and C_6H_6 at 293 K or 298 K and its is found that N_{am}(DRK) and N_{am}(BET) can be slightly different.

As shown in Fig. 1, it appears that Kaganer´s hypothesis is correct, the criteria of temperature invariance of E being satisfied at least over a certain range of temperature T. The adsorption of a number of vapours by carbon black Hoechst and by α-MnO_2, at different temperatures,[25,26] leads to linear plots for the logarithmic representation of Eq. (6). Moreover, in the case of carbon blacks one obtains a single DRK plot by using affinity coefficients similar to those used in the DR equation. The slope leads to a characteristic energy E_0 = 10.8 kJ mol^{-1}, against 10.4 kJ mol^{-1} in the case of Vulcan 3G, another well known and non-porous carbon black. It is interesting to note that these values are close to the empirical value of 11.4 kJ mol^{-1} found in Eq. (2) and corresponding to the limit for very large pores. These observations confirm that Dubinin´s theory is not limited to the adsorption of vapour by microporous solids and further developments can be expected in the framework of the DRK equation.

The Dubinin—Astakhov Eq. (1) is based on a thermodynamic potential, but it has been possible to correlate it with models using adsorption energies derived from intermolecular potentials. A number of studies have been published recently[8,10—12] and an excellent review is presented in the book of Rudzinski and Everett.[27] For example, it is shown within the framework of the so-called condensation approximation, that the normalized DA equation, $\theta_{DA} = \exp[-(A/E)^n]$, results from an integral transform involving a local isotherm $\theta(T,p,\varepsilon)$ and a distribution $\chi(\varepsilon)$ of the gas—solid adsorption energy ε,

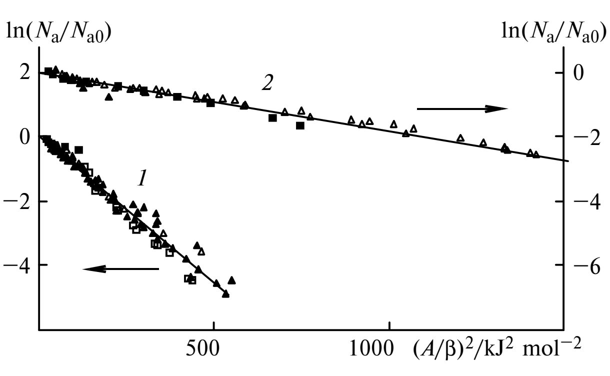

Fig. 1. The Dubinin—Radushkevicha—Kaganer plot for the adsorption of C_6H_6 (282, 293, 311, and 323 K), CCl_4 (293 and 305 K), CH_2Cl_2 (293 K), and N_2 (77 K) on carbon black Hoechst (*1*) and of C_6H_6 (282 K), CH_2Cl_2 (278, 293, and 315 K) and N_2 (77 K) on α-MnO_2 (*2*).

$$\theta_{DA} = \int\theta(T,p,\varepsilon)\chi(\varepsilon)d\varepsilon. \quad (7)$$

It appears that the isotherms of Langmuir, Fowler—Gugenheim and Hill-de Boer can be used as local isotherms to generate the DA isotherm θ_{DA} and in all cases the energy distribution is given by

$$\chi(\varepsilon) = (n/E^n)(\varepsilon - \varepsilon_0)^{n-1}\exp[-(\varepsilon - \varepsilon_0)^n/E^n]. \quad (8)$$

The lower bound ε_0 depends on the local isotherm and expressions are given to calculate it.[27]

In spite of the simplifications used in the condensation approximation, this approach leads to important results, as far as the DA equation is concerned. Firstly, some mathematics show that E is related to the average energy ε_{av} of distribution (8)

$$E = (\varepsilon_{av} - \varepsilon_0)/[\Gamma(1 + 1/n)]. \quad (9)$$

This gives a meaning to the characteristic energy E, in terms of adsorption energies. Secondly, it appears that the assumptions regarding the local isotherms are reasonable. As pointed out by López—Ramón,[28] the initial sections of the model isotherms of CH_4, CF_4, and SF_6 produced by Monte Carlo simulations for adsorption in single slit-shaped carbonaceous micropores at 258—298 K can be represented by the Hill-de Boer isotherm,

$$\theta_{HdB}(T,p,\varepsilon_{HdB}) = 1/\{1 + (K/p)\exp[\theta_{HdB}/(1 - \theta_{HdB}) - (\varepsilon_{HdB} + \theta_{HdB}\omega)/(RT)]\}. \quad (10)$$

In this expression, ε_{HdB} represents the average adsorption energy in the pore, ω is the mean interaction energy between the adsorbed molecules and K depends on the temperature.

The same observation applies, for $\theta < 0.1$—0.2, to the model isotherms obtained for CO_2 adsorbed in pores of 0.4 to 2.4 nm at 273 K and at pressures up to 3.2 MPa. Figure 2 shows the value of $\varepsilon_{HdB}(CO_2, 273\ K)$, as a function of the pore width L, obtained by fitting these isotherms to Eq. (10). The limiting value of 19 kJ mol^{-1} is close to the energy of adsorption of CO_2 on an open graphitic surface and, following the known model,[27] one finds that the lower bound ε_0 = 15 kJ mol^{-1}.

In spite of the shortcomings of the condensation approximation, these observations justify the procedure suggested[29,30] to derive micropore distributions dW/dL from the experimental isotherms by using integral transforms and either the Hill-de Boer or the Fowler—Guggenheim isotherms as local isotherms. (The

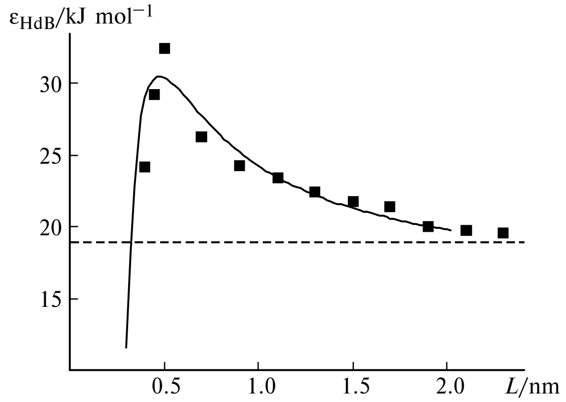

Fig. 2. Variation of the average adsorption energy (ε_{HdB}) for CO_2 adsorbed at 273 K in slit-shaped model pores (L), derived from the model isotherms fitted to the Hill-de Boer Eq. (10).

choice depends on the relative temperature T/T_c). However, nowadays it is easier to derive micropore distributions in terms of weighted contributions of model isotherms resulting from computer simulations.

The approach based on Eqs. (7)—(9) and on modeling provides a better understanding of the foundations of Dubinin's theory, originally based on the thermodynamic potential $A = RT\ln(p_s/p)$, and not on intermolecular potentials.

Adsorption of vapour mixtures

The Dubinin—Astakhov equation is limited to the adsorption of single vapours. Consequently, the Russian School had already considered the extension to mixtures[31] in the early 1950s. In parallel, other approaches have been developed, one of them being the theory of Myers and Prausnitz (MP)[32] presented in 1965. It has been shown recently that the DA Eq. (1) can be combined with this theory, which leads to the Myers—Prausnitz—Dubinin theory (MPD).[15,16] In view of the simplicity of its parameters, Eq. (1) allows better predictions than the isotherms of Langmuir, Freundlich, and Toth, used previously in MP.

Following Myers and Prausnitz, the fundamental requirement for the adsorption equilibrium of several vapours with partial pressures p_i, is the equality of the integrals Ψ_i of the reduced individual isotherms,

$$\Psi_i = \int_0^{p^0} N_i(p)/p\mathrm{d}p\,, \tag{11}$$

where $p^0 = p_i/(x_i^a\gamma_i^a)$. With the DR equation, frequently observed for activated carbons,

$$\Psi_i(p_i) = (W_{0i}/V_{\mathrm{m}i})[\beta_i E_{0i}/(RT)]\pi^{0.5}\times$$
$$\times\{1 - \mathrm{erf}[RT/(\beta_i E_{0i})\ln(x_i^a\gamma_i^a p_{\mathrm{s}i}/p_i)]\}/2, \tag{12}$$

where p_i is the vapour pressure of component (i), x_i^a is its molar fraction in the adsorbed state, and γ_i^a is the corresponding activity coefficient. A similar expression has been derived for the DA Eq. (1) and it is currently being tested for mixed adsorption in zeolites.

In the case of binary mixtures, the equilibrium condition $\Psi_A = \Psi_B$ can be solved easily with the help of a minimum of experimental information, provided that the activity coefficients in the adsorbed phase, $\gamma^a{}_A$ and $\gamma^a{}_B$, are equal to unity (Hypothesis of an ideal adsorbed state, IAS). As shown recently,[33] for benzene and 1,2-dichloroethane (DCE) vapour mixture adsorbed at 293 K by a typical industrial active carbon, the agreement between the calculated and the experimental mole fractions, using the IAS approximation, leads to reasonable agreement in the range $0.3 < x^a < 0.7$. Beyond, one observes deviations due to the non-ideality of the adsorbed state. For a total of $n = 102$ experimental points and using the data for the partial pressures and the mole fractions, one obtains a standard deviation $\sigma = \{\Sigma(\psi_{C_6H_6} - \psi_{DCE})/\psi_{C_6H_6}]^2/n\}^{1/2}$ of 0.13. This agreement can be improved significantly for $x^a < 0.3$ and $x^a > 0.7$, if one introduces the values of the activity coefficients $\gamma^a{}_{C_6H_6}$ and $\gamma^a{}_{DCE}$ derived from the study of the liquid—solid equilibrium. Under these circumstances, $\sigma = 0.08$. Figure 3 shows the correlation between the experimental molar fractions $x^a{}_{C_6H_6}$ and the values calculated from the condition $\Psi_A = \Psi_B$, using the experimental partial pressures and the activity coefficients.

The validation of the new MPD theory has already been carried out for several systems, including the adsorption of vapour mixtures by zeolites. The advantage of combining Dubinin's equation with the Myers—Prausnitz theory is obvious, and Eq. (12) is a welcome extension of Dubinin's theory. This equation has also been used successfully in the case of dynamic adsorption of vapour mixtures over active carbon beds.[13,34]

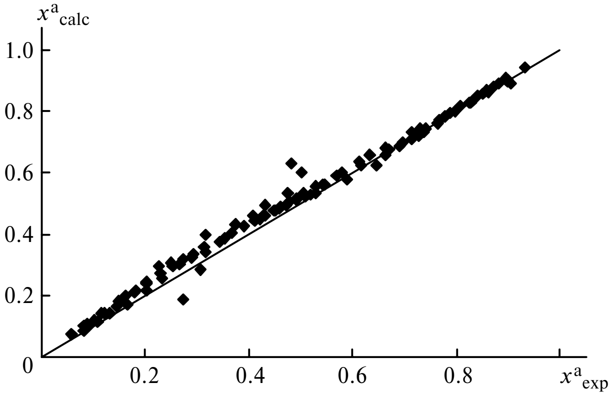

Fig. 3. Correlation between the calculated and experimental compositions ($x^a{}_{calc}$) of benzene vapours adsorbed with 1,2-dichloroethane on a typical active carbon at 293 K. The calculations are based on Eq. (12), using the corresponding equilibrium pressure $p_{C_6H_6}$ and the activity coefficients $\gamma^a{}_{C_6H_6}$ from the solid—liquid equilibrium.

Immersion calorimetry and pore size distributions

Dubinin's fundamental equation (1) relates the amount adsorbed N_a to a thermodynamic potential, $A = RT\ln(p_s/p)$, which implies straightforward consequences. It appears therefore that analytical expressions can be found for the isosteric and net heats of adsorption. The same is true for ΔH_i, the enthalpy of immersion of the solid into a liquid whose vapour is adsorbed according to Eq. (1). In the case of microporous solids, ΔH_i is the integral of the net enthalpy of adsorption, since the term $h_{LV}S_{LV}$ corresponding to the liquid—vapour interface vanishes. One obtains finally[9,14,18]

$$\Delta H_i\ (\mathrm{J\ g^{-1}}) = -\beta E_0(W_0/V_m)(1 + \alpha T)\times$$
$$\times\Gamma(1 + 1/n) + h_i S_e, \qquad (13)$$

where α is the expansion coefficient of the liquid, $\Gamma(1 + 1/n)$ is the tabulated gamma function and h_i (J m^{-2}), a negative quantity like ΔH_i, represents the wetting of the external (non-porous) surface area of the solid, S_e. The latter is conveniently derived from comparison plots based on the adsorption of the standard adsorbates N_2 (77 K), C_6H_6 (293 K) or CO_2 (273 K)[35] on non-porous carbon blacks.

Equation (13) provides useful complementary information on the microporous structure of the solid. In the case of activated carbons of medium and high activation, gate effects are usually absent and ΔH_i reflects the accessibility of the micropore system to the liquid. Using probes with molecular dimensions between 0.35 and 1.5 nm, the combination of adsorption and immersion data leads to pore size distributions. This is illustrated in Fig. 4, for a new microporous carbon black, XC-72-16. The graph shows the histogram derived from the enthalpies of immersion, the distribution predicted by Eqs. (4) and (5) and the results based on the method of CO_2 adsorption at 273 K, analyzed with the help of model isotherms obtained from computer simulations.[22] Similar agreements have been observed for other microporous carbons and, in some cases, the distributions have been confirmed by direct STM observation of the surface.

If gate effects are present, as observed in carbons of low activation or in industrial molecular sieves obtained by blocking partly the pore entrances, ΔH_i provides information on the sieving effect, but not on the internal micropore system. Gate effects may therefore lead to an apparent contradiction between the results obtained from immersion calorimetry and from the adsorption of small molecules, typically CO_2 and CH_2Cl_2. For example, in the case of char C-400 resulting from the pyrolysis of material of vegetable origin near 400 °C (see Table 1), the adsorption of CH_2Cl_2 at 293 K leads to a micropore volume W_0 = 0.13 cm^3 g^{-1} and a characteristic energy E_0 = 26.7 kJ mol^{-1}. For CO_2 at 273 K and at pressures up to 3.2 MPa one obtains W_0 = 0.12 cm^3 g^{-1} and E_0 = 28.4 kJ mol^{-1}, using $\beta(CO_2) = 0.35$.[35] Equation (2) suggests average pore widths L_0 of 0.70 and 0.64 nm, but the experimental enthalpies of immersion into C_6H_6 (0.45 nm) and CCl_4 (0.64 nm) are much smaller than the values predicted by Eq. (13). This means that a gate effect of approximately 0.4 nm excludes the latter molecules from micropores, which should be largely accessible to them. The CO_2 adsorption data for 273 K analyzed with the help of the model isotherms leads to the internal micropore distribution shown in Fig. 5. The average pore size is 0.86 nm, in reasonable agreement with the values suggested by Eq. (2). To our knowledge, it is the first application of computer modeling to the description of the internal microporosity masked by a gate effect. The reality of this system is confirmed by the gradual activation of the char, which exposes and develops the initial microporosity. The plot of the micropore volume W_0, as a function of the degree of burn-off extrapolates to a value close to 0.15 cm^3 g^{-1}.

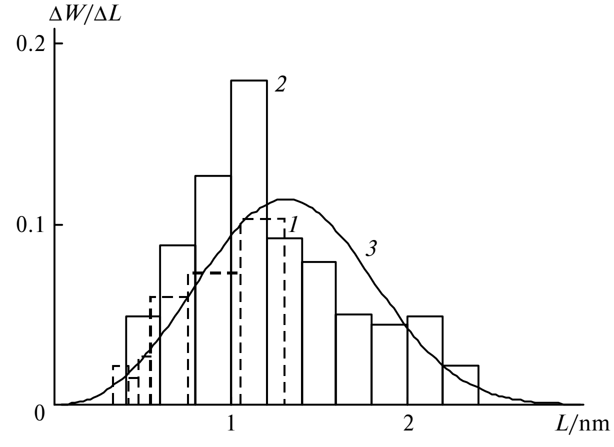

Fig. 4. Micropore distributions in carbon XC-72-16 obtained from immersion calorimetry at 293 K (*1*), computer simulations of CO_2 adsorption at 273 K (*2*), and on Eqs. (4) and (5) (*3*).

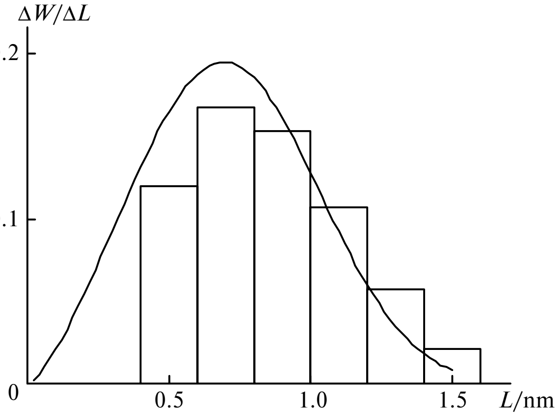

Fig. 5. Internal microporosity of char C-400 derived from the CO_2 adsorption at 273 K, using model isotherms based on Monte Carlo simulations. The curve corresponds to Eqs. (4) and (5).

Adsorption of water by activated carbons

The adsorption of water by microporous carbons has long been considered a separate problem, the isotherm being of type IV or V and not of type I, as observed for the volume filling of micropores by most organic and inorganic adsorbates. By 1981, Dubinin and Serpinski had arrived at a satisfactory model to describe the initial part of the isotherm on the basis of a kinetic model.[36] One of its parameters, the number of primary (hydrophilic) centres a_0 could also be described in terms of the enthalpy of immersion.[7,9]

Following a mathematical analysis, it was shown in the mid-1990s, in collaboration with Dubinin's laboratory,[18,37] that type V isotherm can be represented by Eq. (1). It appears that the shape of the water isotherm is dictated by the relatively low value of the characteristic energy $E(H_2O)$, typically 0.5 to 2.5 kJ mol^{-1} as opposed to 18—25 kJ mol^{-1} for benzene for the same carbons. As a consequence, near room temperature the low value of $E(H_2O)/(RT)$ shifts the inflexion point of the isotherm towards higher relative pressures p/p_s, typically 0.3 to 0.8. The steepness of the curve around the inflexion point is influenced by exponent n which varies between 3 and 7. It was also found that the principle of temperature invariance of E and n, required by Dubinin's theory, is fulfilled over a reasonable range of temperature. Consequently, Eq. (1) can be used to describe the adsorption branch of the water isotherm on active carbons (The desorption branch also follows Eq. (1), but with higher values of $E(H_2O)$ and n). The validity of Eq. (1) is confirmed by the good agreement found between the experimental enthalpies of immersion into water and the values predicted by Eq. (13).

Figure 6 shows the logarithmic DA plot for the adsorption of water by active carbon CM at 275 K and 293 K, where $E(H_2O)$ = 1.95 kJ mol^{-1} and n = 4.15. This new development of Dubinin's theory leads to an interesting correlation between the enthalpies of immersion into water and benzene, on the one hand, and the specific interaction of water with the surface (complexes containing oxygen and basic groups), on the other hand. Eq. (13) suggests that in the absence of specific interactions between water and the surface, the two enthalpies should be proportional and that water has a specific affinity coefficient $\beta(H_2O)$ with respect to benzene. For carbons with variable degrees of oxidation, one obtains the following relation[38] between $\Delta H_i(H_2O)$ and $\Delta H_i(C_6H_6)$,

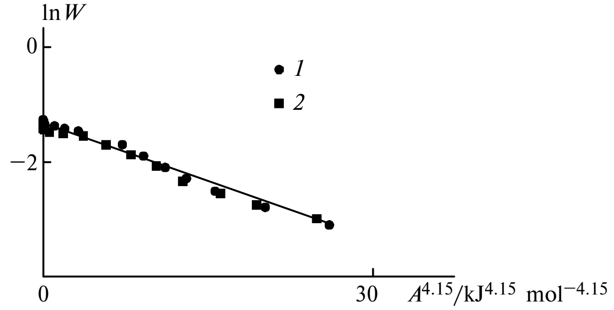

Fig. 6. Logarithmic DA plots for the adsorption of water by carbon CM at 275 (*1*) and 293 K (*2*). Exponent n = 4.15.

$$\Delta H_i(H_2O)\ (J\ g^{-1}) = 0.210\Delta H_i(C_6H_6) - - 9.9([O] + [HCl]). \qquad (14)$$

In this expression, [O] (mmol g^{-1}) and [HCl] (mequiv.HCl g^{-1}) denote the amount of oxygen present on the surface and detected by TPD, and the number of basic groups titrated with HCl. The latter are found to contain only small amounts of oxygen.

It follows that the real affinity coefficient of water relative to benzene, $\beta(H_2O) = 0.057\pm0.007$. As expected, this value is much lower than that observed for most adsorbates, typically 0.33 for nitrogen and 4.05 for tri-2,4-xylylphosphate, a liquid molecule with a critical dimension of 1.5 nm. This reflects the low affinity of water for porous and non-porous carbon. In the absence of oxygen and of basic groups, $\Delta H_i(H_2O)$ should be approximately one fifth of $\Delta H_i(C_6H_6)$, which means that the state of the surface can be assessed from the comparison of the two enthalpies of immersion.

A correlation similar to Eq. (14) is found for methanol and ethanol adsorbed by activated carbons with different degrees of oxidation.[39] The specific interactions are respectively −5.32 and −2.64 J per mmole of oxygen, but the non-specific interactions with the carbon largely dominate.

The fact that water adsorption in activated carbons can also be described in the framework of Dubinin's theory, offers interesting possibilities in the case of mixtures, provided that the vapours correspond to liquids miscible with water. If they are not miscible, it is likely that the same situation will occur in the adsorbed state, and one must consider the model of independent co-adsorption.[40] In this case, each species occupies the micropore volume left free by the other and their adsorption is governed by the individual isotherms (DA for water and DR for the organic vapour). However, if the total volume occupied by the vapours exceeds W_0, water is invariably expelled from the micropore system.

This approach has been applied successfully to the case of dynamic filtration of humid air containing a binary mixture of organic vapours.[40] The calculations combine the MPD model with the model of independent co-adsorption, which requires large computer facilities.

Adsorption from aqueous solutions

Adsorption from aqueous solutions, by activated carbons and other hydrophobic surfaces such as dealuminated zeolites, plays an important role in filtration technology. Attempts have therefore been made to describe the adsorption equilibrium by adapting expressions used for the vapour phase.

Since Dubinin′s theory is based on the thermodynamic potential $A = -\Delta G_{\mathrm{ads}}$, it is possible, in principle, to consider preferential adsorption from solutions by replacing relative pressures p/p_{s} by relative concentrations $c_{\mathrm{eq}}/c_{\mathrm{s}}$. Under these circumstances, the reference state for the adsorbate is no longer the vapour at pressure p_{s} or the corresponding liquid, but the adsorbate in the saturated solution.

It has been shown[8,27,41] that in many cases an expression similar to the DRK Eq. (6) applies. In the present formalism, it corresponds to

$$N_{\mathrm{a}} = N_{\mathrm{am}}\exp\{-[RT\ln(c_{\mathrm{s}}/c_{\mathrm{eq}})/E_{\mathrm{s}}]^2\}, \qquad (15)$$

where N_{am} represents the limiting amount adsorbed and E_{s} is the characteristic energy for the given system.

Surprisingly, the majority of authors dealing with adsorption from solution use adsorption isotherms of the Langmuir, Freundlich, or Redlich type, although their parameters are less predictable than those of Eq. (15). However, if one considers adsorption at one temperature only, the choice between the different expressions is relatively unimportant. On the other hand, if one considers different temperatures, Eq. (15) allows predictions on the basis of simple properties, provided that E_{s} is temperature invariant. This property has not yet been investigated systematically and it was therefore decided to examine in more detail the case of phenol and its homologues, 3-aminophenol, 3-chlorophenol, 4-cresol, and 4-nitrophenol adsorbed from aqueous solutions by activated carbons.[17] In view of its industrial importance, the adsorption of phenolic compounds from aqueous solutions is well documented.

Preliminary investigations show that the requirement for temperature invariance is fulfilled, at least near room temperature. For a given carbon, the adsorption data of the different compounds can be brought in line in the domain $10^{-4} < c_{\mathrm{eq}}/c_{\mathrm{s}} < 1$ by using specific affinity coefficients β_{s} relative to phenol, *i.e.*, $\beta_{\mathrm{s}}(\mathrm{PhOH}) = 1$. This suggests a generalization of Eq. (15),

$$N_{\mathrm{a}} = N_{\mathrm{am}}\exp\{-[RT\ln(c_{\mathrm{s}}/c_{\mathrm{eq}})/\beta_{\mathrm{s}}E_{0\mathrm{s}}]^n\}, \qquad (16)$$

with $n = 4$ for the phenols on different carbons. The corresponding affinity coefficients are presented below.

Adsorbate	β_{s}	Adsorbate	β_{s}
3-Aminophenol	0.84±0.15	4-Cresol	0.87±0.04
3-Chlorophenol	1.03±0.1	4-Nitrophenol	0.84±0.07

It also appears that each carbon is characterized by a value of $E_{0\mathrm{s}}$, relative to phenol, but no correlation has been found with the characteristic energy E_0 relative to benzene, derived from vapour adsorption.

Equation (16) represents another unexpected development of Dubinin′s theory. Its potential is considerable, in particular in relation to co-adsorption and to the enthalpy of adsorption from solution, determined by immersion calorimetry. Further evidence is required and it will be provided by a systematic investigation, currently under way in our laboratory.

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