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RECENT DEVELOPMENTS IN DUBININ'S THEORY

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Abstract—Dubinin's theory, developed in successive stages between 1947 and 1971 and extended to immersion calorimetry in the 1980s, has recently found new applications. It has been shown that water adsorption by microporous carbons, corresponding to type IV and V isotherms, can be described by the Dubinin–Astakhov (D–A) equation. The extension to immersion calorimetry is also valid and provides information on the interaction between water and oxygen-containing surface groups. The D–A equation has also been combined successfully with the theory of Myers and Prausnitz, which leads to a satisfactory description of static and dynamic adsorption of binary mixtures by active carbon beds.

Key Words—A. Activated carbon, C. adsorption, D. microporosity.

1. INTRODUCTION

In 1947, Dubinin and his collaborators published the first papers on the adsorption of vapours by activated carbons and proposed the classical equation of Dubinin and Radushkevich [1–3]. This work set the stage for an original description of adsorption by microporous carbons, and later by other microporous solids such as zeolites [4] and clays [5]. A major advantage of this theory lies in the simplicity of the parameters—readily available physical properties—and in the possibility of predicting the adsorption of a variety of systems, over a relatively wide range of pressures and temperatures.

Retrospectively, it appears that the possibilities offered by Dubinin's idea go far beyond the original expectations of its author. For example, it has been possible to establish a correlation with micropore distributions and to extend the Dubinin's fundamental equation to immersion calorimetry [6]. Consequently, the combination of adsorption and immersion techniques provides a useful tool for the characterization of activated carbons and of microporous solids in general.

Recently, two further applications have been found for Dubinin's theory. Firstly, it has been shown that the Dubinin–Astakhov equation, which generalizes the earlier expression of Dubinin and Radushkevich, can also describe the interaction between water and microporous carbons, with its thermodynamic consequences in the field of immersion calorimetry [7,8]. Secondly, it was shown that Dubinin's theory could be combined with the formal approach of Myers and Prausnitz, to provide an analytical solution to the problem of binary and multiple vapour adsorption by active carbons [9,10]. This approach also rehabilitates an earlier attempt of Bering and Serpinski [11,12] to adapt Dubinin's theory to binary adsorption.

In the present paper, we present these new developments, preceded by a reminder of Dubinin's theory for the volume-filling of micropores [6,13,14].

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2. DUBININ'S THEORY

On the basis of Polanyi's earlier work, Dubinin postulated that the amount N_a of vapour adsorbed by an active carbon, at relative pressure p/p_s, is a function of the thermodynamic potential

$$A = RT \ln(p_s/p) \qquad (1)$$

From the adsorption of simple organic compounds such as benzene, it appeared that a Gaussian expression could be used and a systematic study revealed that the vapour and the solid could be characterized by specific scaling factors. This led to the classical expression of Dubinin and Radushkevich [1–3]

$$N_a = N_{ao} \exp[-B(T/\beta)^2 \log^2(p_s/p)] \qquad (2)$$

where the structural constant B depends on the solid (average micropore size) and β is the affinity coefficient, a quantity depending on the adsorbate. By convention, $\beta(C_6H_6) = 1$. The limiting amount adsorbed in the micropores, N_{ao}, is related to the volume filled by the molecule, $W_o = N_{ao} V_m^a$. Although the molar volume in the adsorbed state, V_m^a, is probably different from the liquid state, as shown recently, it is possible to work with the relative quantities $W/W_o = N_a/N_{ao}$ for different adsorbates and to compare the limiting values W_o.

On the basis of further experiments, in particular with zeolites, Dubinin and Astakhov [4] generalized eqn (2), which now takes the form

$$N_a = N_{ao} \exp[-(A/\beta E_o)^n] \qquad (3)$$

In the case of active carbons, the characteristic

energy E_o is related to the average size of the micropore system and n is a measure of the heterogeneity of the system. For relatively narrow distributions, $n=3$. On the other hand, in the case of strongly activated carbons of industrial origin, with no molecular sieve properties, n can be as low as 1.5 [15,16].

Since eqns (2) and (3) contain a thermodynamic potential, exact relations can be derived for the isosteric and the net heats of adsorption. Moreover, in the case of micropores, the integral of the net heat of adsorption is equal to the enthalpy of immersion into the corresponding liquid. The D–A equation (eqn (3)) leads to [6]

$$\Delta h_i\ (\mathrm{J\ g^{-1}}) = -N_{so}\beta E_o(1+\alpha T)\Gamma(1+1/n) \quad (4)$$

where α is the thermal expansion coefficient of the liquid and Γ is the tabulated Gamma function. For carbons, where n is usually close to 2, eqn (4) becomes

$$\Delta h_i\ (\mathrm{J\ g^{-1}}) = \beta E_o W_o(1+\alpha T)(\pi)^{1/2}/2V_m^a \quad (5)$$

As discussed in detail elsewhere [6,14,17,18], the combination of adsorption and immersion techniques is very useful for the characterization of microporosity in carbons. From a practical point of view, if E_o is known from a single isotherm such as benzene or CH_2Cl_2, the enthalpy of immersion can be used to determine the micropore volume $W_o(L)$ filled by a liquid probe of critical molecular size L. This leads to the volumic distribution of the micropores, $\Delta W/\Delta L \cong dW/dL = f(L)$. With the recent progress made in STM, it is also possible to determine the distribution of the micropore widths from their observed frequencies, $\Delta N/\Delta L \cong dN/dL$. For the latter, approximately 150 micropores were considered.

The distributions obtained for carbon CMS are shown in Fig. 1. They are slightly different, which is not too surprising, in view of the different meanings of these distributions: Two pores of width L, instead of a single pore, are not distinguished in the histogram dW/dL, which considers only their total volume. Although a good overlap of the two distributions has been reported for other active carbons examined by high resolution transmission electron microscopy [19], it appears that there are relatively more narrow micropores in the present case.

3. WATER ADSORPTION AND THE DUBININ–ASTAKHOV EQUATION

In view of the low affinity of water for carbon, one observes usually type III (open graphitic surface) or type V isotherms (micropores). By 1981, Dubinin and Serpinski arrived at a satisfactory model to describe the initial part of these isotherms, on the basis of a kinetic model [20]. The idea was that adsorption begins at hydrophilic primary centres and extends from there through hydrogen bonding. This leads to clusters, which eventually coalesce and explain, partly at least, the hysteresis loop observed on desorption.

An agreement was also found between the number of primary sites and the enthalpy of immersion into water [21,22]. Furthermore, the comparison with TPD (temperature-programmed desorption) suggested that for carbon blacks and for typical carbons activated at 850–900°C, the primary centres are probably of the carbonyl type. The Dubinin–Serpinski equation has also been improved by Barton *et al.* [23,24].

Recently [7], a mathematical analysis revealed that the D–A equation (eqn (3)) is S-shaped, but the inflexion point is never observed for isotherms of type I, corresponding to the filling of micropores by most vapours. On the other hand, as illustrated by Fig. 2, modelling shows that the isotherm changes from type I to type V when the energy $E=\beta E_o$ decreases from typical values around 20 kJ mol^{-1} to 1–2 kJ mol^{-1}. It also appears that the slope of the isotherm at the inflexion point depends on the exponent n, which can vary from 2 to 7.

A systematic study of water-active carbon systems, determined at different temperatures showed that the individual isotherms of type V could be fitted to the D–A equation (eqn (3)). Moreover, it appeared that parameters n and E (preferred to βE_o) are relatively constant over a certain temperature range, as required by Dubinin's theory. This is illustrated by the charac-

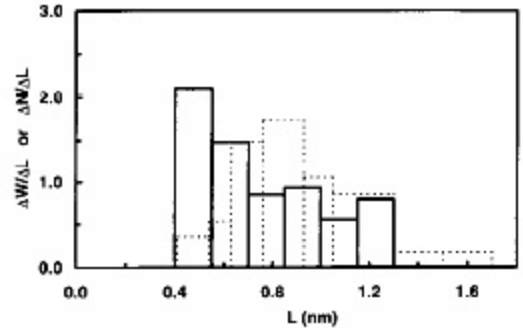

Fig. 1. Micropore distributions in active carbon CMS, obtained from molecular sieve experiments, $\Delta W/\Delta L$ (dotted line), and from STM analysis, $\Delta N/\Delta L$ (solid line).

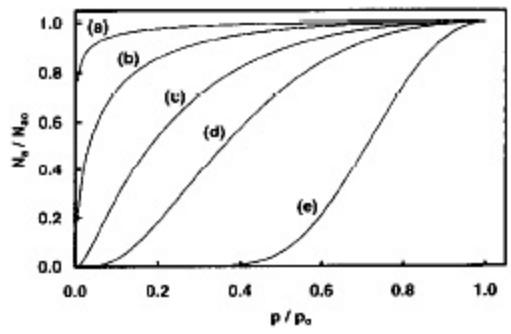

Fig. 2. Model isotherms corresponding to the D–A equation (eqn (3)), with $T=293$ K, $n=2$, and $E=\beta E_o$ equal to (a) 25, (b) 10, (c) 5, (d) 3 and (e) 1 kJ mol^{-1}.

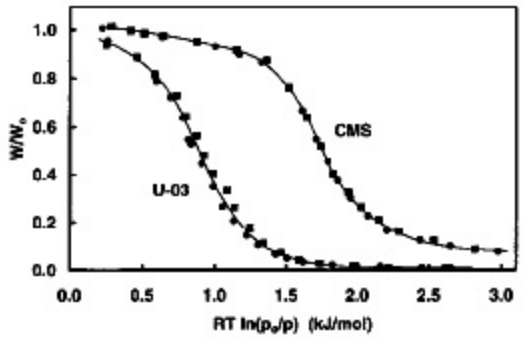

Fig. 3. Characteristic curves for the adsorption of water by active carbons CMS at 275 and 293 K (●,■) and U-03 at 263 and 293 K (●,■).

teristic curves obtained for carbons U-03 and CMS (Fig. 3). A similar observation had been reported earlier by Hassan *et al.* [25] for the adsorption of water by active carbon BPL between 288 and 308 K, but no conclusion was drawn.

Figure 4 shows the data for carbon U-03 in the linearized form of the D–A equation (eqn (3)) and it is interesting to point out that the best fit is obtained by using the molar volume of supercooled water for 263 K, rather than of ice. This indicates that the adsorbed state is still in a liquid-like state at this temperature.

A direct consequence of the temperature invariance of parameters E and n is the relatively good agreement found between the enthalpies of immersion into water calculated from eqn (4), using parameters N_{ao}, E and n of the isotherms, and the experimental values (see Table 1).

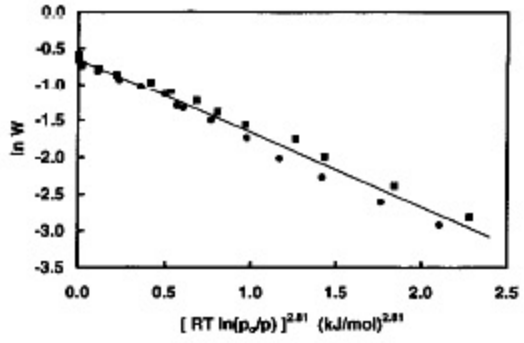

Fig. 4. Logarithmic D–A plot for the adsorption of water by active carbon U-03 at 263 and 293 K (●,■).

More recently [8,26], attention has been focused on active carbons subjected to oxidation, for which the water adsorption is of type IV. This behaviour is related to the different oxygen-containing groups created on the surface and is discussed in more detail below. A typical example of a type IV water adsorption isotherm observed for carbons CMS treated with HNO_3, is shown in Fig. 5. At low pressures ($p/p_s < 10^{-3}$), the isotherm displays an initial section of the so-called Langmuir type, reflecting the saturation of oxygen-containing groups by water. The overall isotherm can be decomposed into contributions of type I and of type V. Since the requirement of temperature invariance is fulfilled, the contributions of the two sub-isotherms to the enthalpy of immersion can be calculated from eqn (4), using the sets of parameters $N_{ao}(I)$, $E(I)$, $n(I)$ and $N_{ao}(V)$, $E(V)$, $n(V)$. As shown in Table 2, one obtains a good correlation between the experimental and calculated enthalpies of immersion into water.

The detailed study of this system also revealed the importance of attaining the true adsorption equilibrium of water, in particular on oxidized active carbons. This is illustrated by Fig. 6, showing isotherms (A) and (B), obtained respectively in 10 days and 9 weeks. Adsorption being very slow, especially at low relative pressures, it appears retrospectively, that the real equilibrium was not attained in the first case. This is also confirmed by the low values of the calculated enthalpy of immersion into water, $\Delta h_i(H_2O) = -29\ J\ g^{-1}$, suggested by the decomposition of the overall isotherm in contributions of type I and V. In the case of isotherm (B), also

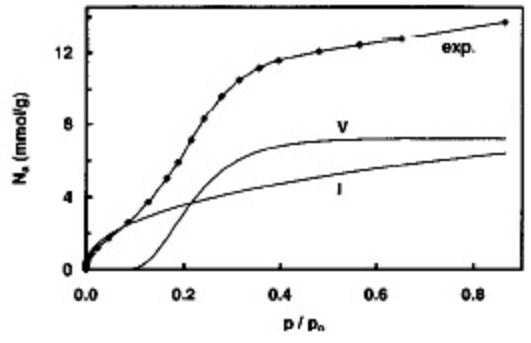

Fig. 5. The adsorption isotherm of water on carbon CMS-ox at 293 K and its decomposition into contributions of types I and V.

Table 1. Parameters for the adsorption of water by typical and untreated active carbons (type V isotherms)

Carbon	T(K)	E(kJ mol^{-1})	W_o(cm^3 g^{-1})	n(J g^{-1})	$-\Delta h_i$ (eqn (4))(J g^{-1})	$-\Delta h_i$ (exp)(J g^{-1})
CMS	293	1.86	0.24	4.20	27	27
	275	2.01	0.27	4.12	–	–
U-03	293	0.87	0.52	2.67	28	32
	263	0.98	0.50	2.94	–	–
N-125	293	1.17	0.57	4.22	31	32
ALCA	293	2.23	0.45	7.67	49	44
MSC-V	293	2.39	0.17	3.28	19	23

Table 2. Parameters for water adsorbed on oxidized active carbons. The type IV isotherm is decomposed in contributions of types I and V following eqns (3) and (4). For series AZ46 [26], only 3 samples are described

Carbon	Initial section (type I)				Second section (type V)				
	n(I)	E(I) (kJ mol^{-1})	N_{ao}(I) (mmol g^{-1})	$-\Delta h_i$(I) (J g^{-1})	n(V)	E(V) (kJ mol^{-1})	N_{ao}(V) (mmol g^{-1})	$-\Delta h_i$(V) (J g^{-1})	$-\Delta h_i$ tot/exp (J g^{-1})
CMS-ox	1.06	6.00	6.71	42	4.73	4.07	7.20	28	70/86
CEP	1.00	7.00	1.24	7.4	2.70	2.20	6.5	13.5	21/20
AZ46-0	0.89	7.54	2.52	21.4	3.19	1.74	14.7	24.3	46/32
AZ46-3	1.08	6.80	4.90	34.4	3.01	2.80	12.7	34	68/79
AZ46-24	1.29	6.91	9.55	65	3.00	3.36	9.3	30	95/95

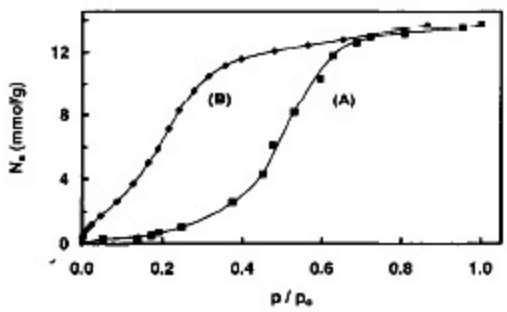

Fig. 6. The adsorption of water by carbon CMS-ox at 293 K achieved in 12 days (A) and in 9 weeks (B). The latter, also shown in Fig. 5, is close to the real equilibrium.

shown in Fig. 5, the data of Table 2 leads to $\Delta h_i(H_2O) = -70$ J g^{-1}, in much better agreement with the experimental value of -86 J g^{-1}. This suggests that isotherm (B) is closer to the real adsorption equilibrium.

This observation leaves open the question about the reliability of earlier type IV water isotherms, which could be cross-checked easily with a single immersion experiment.

The slow adsorption kinetics observed for oxidized carbons, in particular at low pressures, may be due to the formation of clusters or bridges of water around oxygen-containing sites located at the micropore entrances. This may reduce considerably the diffusion of water into the pores, to fill them or to reach other sites.

The correlation between water adsorption at low pressures and the saturation of surface groups has been examined recently in collaboration with Moreno-Castilla *et al.* [26]. An active carbon, derived from olive stones, was oxidized to various degrees with $(NH_4)_2S_2O_8$ and seven samples were obtained (series AZ46). They were fully characterized by adsorption and immersion techniques including water, by TPD and by titration following Boehm's method [27].

It appears that the initial section of the isotherm corresponds to the saturation of the carboxyl, lactone, phenol and basic groups, whereas the type V section still corresponds to the initial carbonyl groups. The adsorption and immersion calorimetry data were subjected to a mathematical analysis (multiple linear regressions), leading to the data given in Table 3. It

Table 3. The interaction of water with surface groups. Values derived from the study of a series of seven active carbons oxidized to various degrees with $(NH_4)_2S_2O_8$ [26]

Surface group	Carboxyl	Lactone	Phenol	Base
Water molecules per group	2.8	2.7	1.4	1.6
Contribution to $-\Delta h_i$ (J mmol^{-1} H_2O)	6.2	6.5	6.8	6.3

appears that carboxyl and lactone groups are practically surrounded by three water molecules, against approximately 1.5 for phenols and bases. On average, the contribution to $\Delta h_i(H_2O)$ is approximately -6.5 kJ per mole of water saturating these groups, thus suggesting a similar type of interaction.

4. BINARY AND MULTIPLE ADSORPTION OF VAPOURS BY ACTIVE CARBONS

4.1 *Static adsorption*

Dubinin's approach provides a satisfactory description for the adsorption equilibrium of single vapours, and it has been extended to their removal from air under dynamic conditions and in PSA. However, the case of binary and multiple adsorption remained a challenge, following the limited success of an extension of the D–R equation (eqn (2)) to binary systems, proposed by Bering and Serpinski in the early 1950s [11,12]. As it appears now, these authors used an unsatisfactory subsidiary equation to solve the problem of binary adsorption and their approach was practically abandoned.

In 1965, Myers and Prausnitz proposed a general formalism to deal with the adsorption equilibrium of two or more components between the vapour phase and the solid [28,29].

Their approach led to a general criterion for equilibrium, summed up by the condition that

$$\Psi_1 = \Psi_2 = \ldots \Psi_i \qquad (6)$$

For each component of the mixture, the function Ψ is related to the adsorption isotherms of the pure component, $N_i(p)$ by

$$\Psi_i = \int_0^{p_i^\circ} N_i(p)/p \, dp \qquad (7)$$

By analogy with the case of liquid mixtures, the partial vapour pressures p_i are related to formal reference states p_i^o of the adsorbates by eqn (8)

$$p_i = x_i^a \gamma_i^a p_i^o \quad (8)$$

where x_i^a is the mole fraction in the adsorbed phase.

It is assumed, to a first approximation, that the adsorbed mixture is ideal and therefore the activity coefficients γ_i^a are equal to unity. As shown recently, this is not the case, even for mixtures such as dichloroethane + benzene, which forms an ideal liquid mixture. However, it appears that assuming an ideal adsorbed state is usually a reasonable first approximation.

As shown by Lavanchy *et al.* [9], it is possible to find an analytical solution to eqn (7), when using the D–R and the D–A equations (eqns (2) and (3)). The former, corresponding to adsorption by typical active carbons, leads to

$$\Psi_i(p_i^o) = (W_{oi}/V_{mi})(\beta_i E_{oi}/RT)(\pi)^{1/2} \times \{1 - erf[(RT/\beta_i E_{oi}) \ln(p_{si}/p_i^o)]\} \quad (9)$$

where *erf* is the classical error function.

If the active carbon shows no molecular sieve effects with respect to the different adsorbates, parameters $W_{oi} = W_o$ and $E_{oi} = E_o$. For binary adsorption, the individual amounts adsorbed at equilibrium can be calculated from the condition that $\Psi_1(p_1^o) = \Psi_2(p_2^o)$, combined with eqn (8) and the mass-balance in the system. For multiple adsorption, on the other hand, one can use the iterative procedure proposed by Valenzuela and Myers [29].

The new approach has been given the names of Myers, Prausnitz and Dubinin (MPD). As discussed in detail elsewhere [9,10], it has been applied successfully to a number of systems. Figure 7 shows the correlation between total amounts adsorbed N_a^{tot}, calculated with the MPD approach, and the experimental values. Similar correlations are observed for the individual amounts adsorbed, with deviations at low concentrations. These deviations are due to the activity coefficients γ_i^a, which may be important in the region of Henry's law. For example, in the case of the system 1,2-dichloroethane + benzene at 293 K, which is ideal in the liquid state. From complementary measurements on the liquid–solid equilibrium, it appears that $\gamma^a(C_6H_6) < 1$, as suggested by the comparison between MPD and the experimental values of the amounts adsorbed $N^a(C_6H_6)$. By symmetry, $\gamma^a(C_2H_4Cl_2) > 1$.

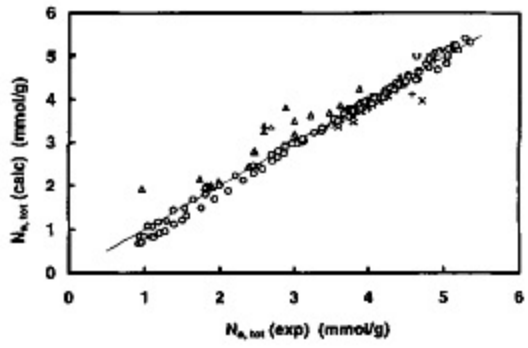

Fig. 7. Correlation between the total amounts of vapours adsorbed by typical active carbons, calculated by the MPD approach, and the experimental values. The data corresponds to five different binary mixtures.

4.2 *Dynamic adsorption*

As shown by Ladugie *et al.* [30], the Dubinin equation can be used in a computer simulation developed for the modelling of adsorption of single vapours by active carbon beds under dynamic conditions. In view of the good results obtained by this approach, the MPD formalism was included in the model. A systematic investigation, reported recently [31], shows that this ab initio approach can be used to predict with good accuracy the dynamic behaviour of binary vapour mixtures in a stream of air, when passing over active carbon beds. Recently, success has also been obtained with the breakthrough curves of the ternary mixture of 2-chloropropane + chlorobenzene + carbon tetrachloride vapours at 298 K. This means that it is possible to predict multiple adsorption and therefore to design filtration systems accordingly. It is also interesting to point out that the approximation of an ideal adsorbed phase has, surprisingly, little influence on the prediction of the dynamic process.

The main advantage of the MPD approach lies in the simplicity of Dubinin's equation, which only requires standard physical properties of the vapours and of the solid. For other expressions, such as the isotherms of Langmuir or Toth [29], the predictions are more difficult, because the specific parameters cannot always be estimated accurately.

In view of the success obtained with the Dubinin equation in single-component Pressure-Swing Adsorption [32], the new MPD formalism is now being adapted to this technique and results will be presented in due course.

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