

DUBININ'S THEORY: A VERSATILE TOOL IN ADSORPTION SCIENCE

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The paper presents the main features of Dubinin's theory for the volume-filling of micropores, its direct consequences in the field of immersion calorimetry and recent developments such as the possibility to describe type V isotherms (water on active carbons) with the Dubinin-Astakhov equation, and to deal with multiple adsorption under static and dynamic conditions. It also confirmed that in some cases Dubinin's theory applies to adsorption by non-porous surfaces.

Ce travail présente la théorie de Dubinin, ses conséquences en calorimétrie d'immersion ainsi que des développements récents. En particulier, la description des isothermes de type V par l'équation de Dubinin-Astakhov (vapeur d'eau sur les charbons actifs) et la combinaison avec la théorie de Myers et Prausnitz qui conduit à une description de l'adsorption multiple en régimes statique et dynamique. La théorie de Dubinin inclut également l'adsorption de vapeurs par certains solides non poreux.

1. The origins of Dubinin's theory and its basic features

Formulated in successive stages between 1947 and 1971, Dubinin's theory [1,2] occupies a special place among the various approaches available today for the description of physical adsorption [3]. The major advantage of this theory and of its recent developments is the limited number of parameters required to describe and to predict the adsorption of single vapours and of mixtures, under static and dynamic conditions [4,5]. In spite of its relatively simple formulation, Dubinin's theory is still of great relevance in the field of filtration technology. Our paper presents the background and the developments of this approach, formulated more than 50 years ago.

Dubinin's theory is based on the idea of a simple correlation between the amount adsorbed and the thermodynamic potential $A = RT \ln(p_s/p)$. It is equal to $-\Delta G$, the Gibbs free energy of transfer from the liquid at temperature T and saturation pressure p_s , to the adsorbed state at the same temperature and equilibrium pressure p.

This approach applies essentially to the filling of micropores, but adsorption by certain non-porous surfaces can also be included in this description. Dubinin's work showed that in the case of organic vapours adsorbed by active carbons, the mathematical relation is a Gaussian and one obtains a single curve when plotting the relative amount adsorbed N_a/N_{am} as a function of A. Moreover, it appeared that for a given carbon, the curves corresponding to different adsorbates are affine. Therefore, by using specific parameters β called affinity coefficients, it is possible to reduce the adsorption data for a given solid to a single curve. By convention, benzene is the reference vapour and $\beta(C_6H_6) = 1$. The influence of the solid itself is expressed by a specific parameter E_o , called the *characteristic energy* of the solid.

Further work carried out with solids such as zeolites showed that the following relation, known as the Dubinin-Astakhov (DA) equation, applies

$$N_a = N_{a0} \exp[-(A/\beta E_0)^n] \quad (1)$$

The adsorption process implied by equation (1) corresponds mainly to the filling of micropores (widths of less than 2 nm). Provided that these pores are equally accessible to the molecular probes, their total volume W_0 corresponds to the limiting amount adsorbed N_{a0} multiplied by V_m , the molar volume of the adsorbate in the liquid state. Reduced accessibility, often associated with increasing molecular size of the probes, reflects either the micropore size distribution [2] or the presence of a gate effect at the entrance of the pores [6].

Although the DA equation was derived on empirical grounds, it has been shown that it can be associated with an energy distribution [2,3]. For example, equation (1) may be expressed as an integral transform involving a Langmuir core and the adsorption energy distribution.

$$\chi(\epsilon) = n(\epsilon - \epsilon_0)^{n-1} (\beta E_0)^{-n} \exp[-\{(\epsilon - \epsilon_0)/\beta E_0\}^n] \quad (2)$$

Mathematical modelling can therefore lead to the corresponding micropore distributions and provide interesting information on the meaning of the fundamental parameters. However, it is easier to derive the pore size distributions from adsorption experiments or immersion calorimetry (see below), using molecular probes with sizes between 0.4 and 1.5 nm [2,6]. In the case of microporous carbons, such experiments have also led to a useful correlation between the characteristic energy E_0 and the average width L of ideally slit-shaped pores [2].

Although the DA equation applies essentially to microporous solids, it appears that adsorption by certain non-porous surfaces follows equation (1) with exponent $n=2$. This corresponds to the equation of Dubinin, Radushkevich and Kaganer (DRK) [3],

$$N_a = N_{a0} \exp\{-[RT \ln(p/p)/E]^2\} \quad (3)$$

Stoekli, Hugi-Cleary and Centeno [7], have shown that this equation applies to the case of dichloromethane adsorbed on non-porous α -MnO₂ at different temperatures. This is confirmed by more recent data obtained with benzene (298 K) and nitrogen (77 K). As shown in *figure 1*, a single DRK plot is obtained in the range $5 \text{ kJ mol}^{-1} < A < 28 \text{ kJ mol}^{-1}$, by using specific affinity coefficients β of approximately 0.7 (CH₂Cl₂) and 0.3 (N₂) relative to benzene.

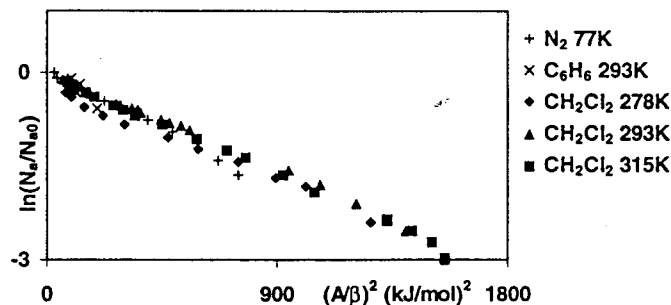


Figure 1. DRK plot for the adsorption of C₆H₆ (293K), CH₂Cl₂ (278, 293, 315K) and N₂(77K) on non-porous α -MnO₂. $E = 15.2 \text{ kJ mol}^{-1}$ for benzene.

These results suggest that the requirement of temperature invariance is fulfilled, at least in the temperature range considered here, and that the principle of affinity also applies. This means that the DRK behaviour observed here also corresponds to the energy distribution (2). It also appears that the limiting amounts adsorbed N_{a0} are in good agreement with the BET monolayer capacity N_{am} derived from the same isotherms, at higher relative pressures.

2. Calorimetric consequences of Dubinin's theory

In view of the temperature invariance of parameters E_0 and n , observed over a wide range of temperatures and relative pressures, interesting thermodynamic consequences can be derived from the DA equation (1). As shown elsewhere [2], one obtains the following expression for the isosteric heat of adsorption q^{st} as a function of degree of micropore filling θ

$$q^{st} = \beta E_0 [(\ln 1/\theta)^{1/n} + (\alpha T/n)(\ln 1/\theta)^{1/n-1}] + \Delta H_{vap} \quad (4)$$

where α is the thermal expansion coefficient of the adsorbate. From this relation, it is possible to derive an expression for the enthalpy of immersion of a microporous solid into a liquid whose vapour adsorption follows the DA equation,

$$-\Delta h_i \text{ (J/mole)} = \beta E_0 N_{a0} (1 + \alpha T) \Gamma(1 + 1/n) \quad (5)$$

where Γ is the tabulated *Gamma* function. For active carbons, n is close to 2, which corresponds to the classical equation of Dubinin and Radushkevich. Often, these solids also have an external (non-microporous) surface S_e . Its contribution to Δh_i is $h_i S_e$, where h_i (J/m²) is the specific enthalpy of immersion into the given liquid.

As shown elsewhere [2,7] the approach based on immersion calorimetry, either alone or combined with adsorption techniques, leads to a good characterisation of active carbons. Typical micropore distributions have also been correlated with direct observations in electron microscopy at high resolution [2] and by STM (Scanning Tunnelling Microscopy) [7].

3. Extension to isotherms of types V and IV

Traditionally, the DA equation (1) is used to describe adsorption related to type I isotherms (microporous solids), or the early stage of type II (DRK mode). Systems described by convex isotherms, were considered outside the framework of Dubinin's theory. This was the case for water on active carbons and therefore Dubinin and Serpinski developed a kinetic model to describe this system [2,8].

Recently, it has been shown by Stoekli, Jakubov and Lavanchy [9] that the DA equation (1) is S-shaped, but the inflexion point occurs at such low pressures that is never observed for type I isotherms. On the other hand, one observes a gradual change from type I to type V when the quantity $E = \beta E_0$ decreases from 20 to 1-2 kJ mol⁻¹. In a systematic study of water adsorption on active carbons, the data could be fitted to a DA equation with n varying from 2 to 7 and the requirement for temperature invariance was satisfied in the range 263 to 300 K. This is shown in *figure 2*, for the adsorption of water by carbon CMS at 275 and 293 K.

This new description is confirmed by the good correlation observed between the values of the enthalpies of immersion calculated with the help of equation (5) - a thermodynamic consequence of Dubinin's theory - and experimental values.

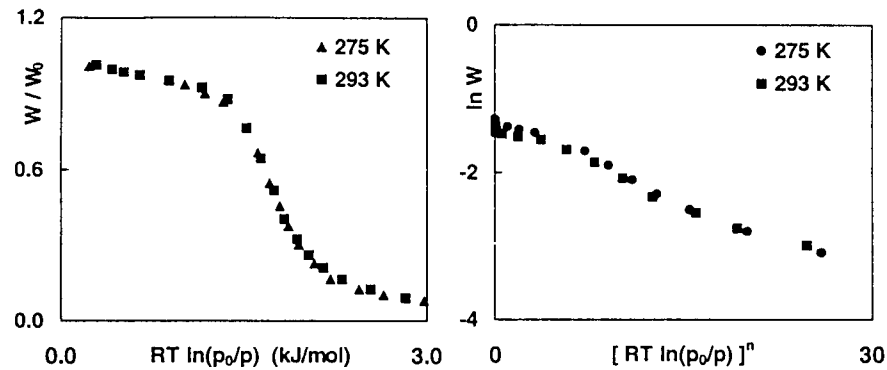


Figure 2. The adsorption of water by active carbon CMS at 275 and 293 K. Characteristic curve (left) and its linearized form (right). Exponent $n = 4.17$.

It has also been established that in the case of carbons with some degree of oxidation, where adsorption corresponds to a type IV isotherm, the overall isotherm can be expressed as the superposition of type I and type V contributions [10,11]. Both fulfil the requirement of temperature invariance of their specific parameters N_{a0} , E and n . Moreover, a correlation has been established between the parameters of the initial section and the various chemical groups present on the surface and identified by titration techniques [11].

The possibility to describe water adsorption within the framework of Dubinin's theory has great advantages in the prediction and the modelling of adsorption by active carbons, as discussed below. At the same time, this opens new perspectives by including formally adsorption isotherms of types IV and V in the formalism of Dubinin's theory, but with the drastic requirement for temperature invariance. The latter must therefore be verified and its domain of validity must be established. (At this stage it should be pointed out that this analysis has not been performed systematically in the past and it is likely that a number of systems are not truly described by Dubinin's theory).

4. Dubinin's theory and the adsorption of mixtures

At an early stage, the Russian school of Dubinin tried to adapt the theory to the case of binary mixtures, but the attempt failed, because of the wrong choice of a subsidiary equation required to solve the problem. Recently, Dubinin's theory has been combined successfully with the formalism developed by Myers and Prausnitz [12] to provide a description for the adsorption of vapour mixtures by microporous solids. As described elsewhere [4,5], if the DA equation (1) applies for the individual isotherms, the adsorption equilibrium requires that the following functions must be equal for the various components (i) of the mixture,

$$\Psi_i = (W_{0i}/V_{mi})(\beta E_{0i}/RT)(1/n)\Gamma [1/n; ((RT/\beta_i E_{0i})\ln(p_{si}x_i/p_i))]^n \quad (6)$$

Γ is the *incomplete Gamma function*, x_i is the mole fraction of species (i) in the adsorbed phase (supposed to be ideal to a first approximation) and p_i its equilibrium pressure.

The MPD approach has been tested successfully with a variety of systems and, in view of the good agreement observed under static equilibrium conditions, it has been considered within the framework of a model presented by Ladugie *et al.* to describe adsorption by carbon beds under dynamic conditions [13]. This simulation model had already been applied successfully with the Dubinin equation to the case of single vapour adsorption from a stream of air. As described elsewhere [5], the model has been extended to binary and ternary mixtures by including the general condition (6). A typical result is shown in *figure 3, left*, for the breakthrough of a ternary mixture of carbon tetrachloride, chlorobenzene and 2-chloropropane in a stream of air over an active carbon bed at 298 K. The calculated curves agree very well with the experimental data, which illustrates the possibilities of this approach.

More recently, we have established that the Dubinin equation (1) can also be used in the case of *independent co-adsorption* of vapours corresponding to immiscible liquids such as water and an organic compound. Under these conditions, the MPD approach is no longer valid, but one may assume, to a first approximation, that each component is adsorbed according to its DA equation (1) in a micropore volume W_0 reduced by the volume occupied by the other component. For the organic vapour and for water one obtains respectively

$$W_1 = N_{a1}V_{m1} = (W_0 - W_2)\exp[-(A_1/E_1)^{n_1}] \quad (7)$$

$$W_2 = N_{a2}V_{m2} = (W_0 - W_1)\{(1-\theta)\exp[-(A_{21}/E_{21})^{n_{21}}] + \theta \exp[-(A_{22}/E_{22})^{n_{22}}]\} \quad (8)$$

Indices 21 and 22 refer to the type I and V contributions to the overall isotherm and θ is the fraction of water adsorbed as type V isotherm.

In spite of its simplicity, this approach is a good approximation for the description of *independent co-adsorption* and it has been included successfully in the computer simulation for dynamic conditions. *Figure 3, right* shows the agreement between the calculated and the experimental breakthrough curves for water (80% humidity) and 2-chloropropane (inlet concentrations c/c_s of 0.001, 0.003 and 0.008), in air at 298 K and over an active carbon bed.

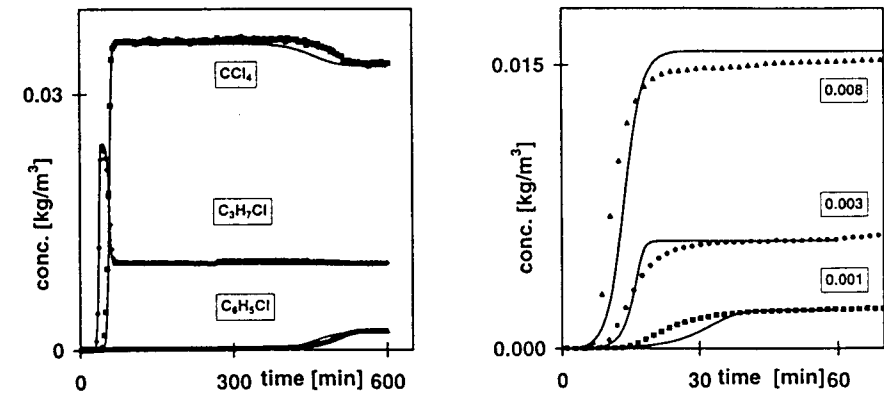


Figure 3. Breakthrough curves for a mixture of carbon tetrachloride, chlorobenzene and 2-chloropropane (left), and for water (80% humidity) and 2-chloropropane at different concentrations (right), in a stream of air over an active carbon bed at 298K. Calculated curves (lines) and experimental data (points).

5. Conclusions

From the recent developments of Dubinin's theory presented here, it appears that, in spite of its simplicity, this approach has not lost its interest under present conditions. Firstly, it is interesting to realise that a variety of systems involving microporous and non-porous solids are described by the fundamental equation of Dubinin and Astakhov and that they fulfil the requirement of temperature invariance. This means, basically, that these systems correspond to adsorption energy distributions of the type given by equation (2). However, this does not alter the well-known fact that the theory does not include the region of Henry's law.

Secondly, it appears that the MPD approach is of great relevance to filtration technology. In this context, the simplicity of the parameters required by Dubinin's theory is a great advantage for the prediction of adsorption under static and dynamic conditions, over a wide pressure and temperature range. As illustrated here, *ab-initio* calculations for removal of vapours from a stream of air are in excellent agreement with the experimental data.

6. References

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