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Commentary on the paper "On the adsorption affinity coefficient of carbon dioxide in microporous carbons" by E.S. Bickford et al. (Carbon 2004; 42: 1867–71)

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The recent letter to the editor by Bickford et al. [1] discusses the uses of the CO_2 affinity coefficient in microporous carbons, β_{CO_2}, and its physical significance. The paper points out the lack of having absolute β values and attempts to give answer to the question of the suitability of the value of $\beta_{CO_2} = 0.35$ in microporous carbons. The authors conclude that this cannot be considered a "classical" value and that much more work is needed to clarify its physical significance, in order to maintain the well-deserved popularity of the Dubinin–Radushkevich equation.

We welcome the effort of the authors to address – and even challenge – the use of β_{CO_2} to characterize microporous carbons. However, we cannot agree with their conclusions. Firstly, because we feel that the importance and relevance of β has been overestimated in the paper.

Secondly, because, on the basis our own research, a suitable classical value of β_{CO_2} near 0.35 appears to exist. Thus, we have reported excellent agreements on the characteristic curves of different carbons, obtained with many couples comparing CO_2 and benzene and or N_2 adsorption. In all the cases, values near 0.35 for CO_2 and 0.33 for N_2 have been used. We wish to address the following three issues.

1. The concern about β_{CO_2} and Dubinin's theory

The uncertainties claimed by the authors should not introduce unsupported concerns about the popularity and general use of Dubinin's theory for the volume filling of micropores (TVFM). The so-called affinity coefficient β is only an experimental shifting factor, which allows the superposition of the characteristic curves of various adsorbates with the curve of benzene. This scaling factor is only a parameter among other parameters found in Dubinin's theory. The authors' concern about β makes sense, but does not differ from that associated with other parameters used in adsorption, such as real adsorption equilibrium, choice of the linear range of the DR and hence micropore volume assessment, density, molecular cross section, etc. To support their concern about β_{CO_2}, the authors present Fig. 1 stating that "If it is indeed an affinity coefficient, it should be able, for example to account for the published results (Bickford's Ref. [4,5]) compiled in Fig. 1". This figure is not a suitable example because the use of β_{CO_2} should always correspond to the basic concepts of Dubinin's theory:

(i) Dubinin's fundamental equation expresses a distribution of the filled volume of the adsorption space with respect to the differential work of adsorption and it is only valid, in principle, at adsorption temperatures below T_c (there exists an expression for the limiting pressure or fugacities, but in a limited temperature range above T_c).
(ii) The constant value of the parameter β (or that of the ratio of the differential molar work of adsorption of a given vapor to the differential molar work of adsorption of the standard) is only true for equally filled volumes of the adsorption space. Moreover, significant differences in the accessibility of the PSD and/or activated diffusion lead to unrealistic characteristic energies E and consequently to meaningless values of $\beta = E/E_o$. It follows, that the

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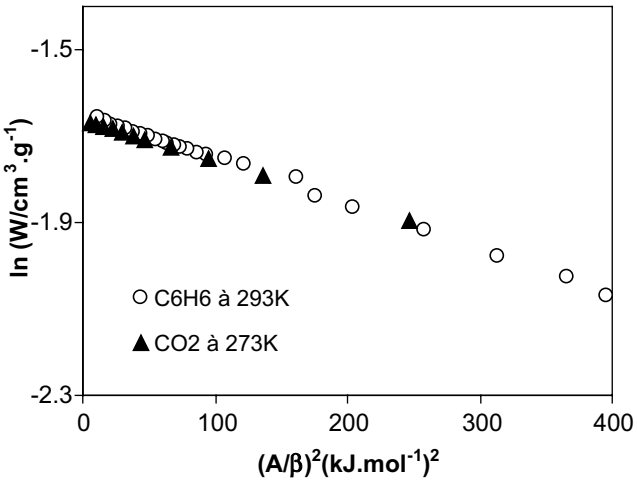

Fig. 1. DR plot for the adsorption of CO_2 and C_6H_6 by carbon MSC-V ($E_o = 31\,kJ\,mol^{-1}$ and best fit for $\beta_{CO_2} = 0.35$).

characteristic curve of two adsorbates should only be compared for the same range of micropore filling θ the adsorbate being in a liquid-like form and preferably at temperatures below T_c. Carbons with strong molecular-sieve effects must be analyzed separately.

None of these points can be applied to Fig. 1 of Bickford et al.'s paper. In addition, the way used to express the results and the experimental conditions used for nitrogen and methane are not the most suitable for comparison purposes because (i) the adsorption uptake is expressed in $mmol\,g^{-1}$ (for comparison purposes it should be in liquid volumes) and (ii) methane and nitrogen are adsorbed at a temperature above their critical temperature hence the saturation pressure has to be calculated using different approaches. As a result, this figure is not the most suitable way for reaching conclusions about β_{CO_2}. Instead of Fig. 1, a DR (or DA) plot would look much nicer and it might reveal that these adsorbents do not necessarily consider the same degree of pore volume filling θ. Our Fig. 1 shows the reliable case of C_6H_6 (293 K) and CO_2 (273 K) adsorbed under similar conditions, as far as θ is concerned. Using molar volumes of 88.9 and $42.8\,cm^3\,mol^{-1}$, one obtains an excellent overlap of the DR plots with $\beta_{CO_2} = 0.35$ ($E_o = 31\,kJ\,mol^{-1}$).

2. Regarding a suitable value for β_{CO_2} to characterize microporous carbons

A careful analysis of the data quoted by the authors in their Table 1 reveals interesting features as far as the origin of the various β_{CO_2} values is concerned.

Firstly, Bickford's Refs. [8,11,21,30] are based on the direct comparison of CO_2 and C_6H_6 isotherms, so that the definition $\beta_{CO_2} = E_{CO_2}/E_o$ clearly applies. For all these carbons, including oxidized samples given in Bickford's Ref. [21], one obtains

$\beta_{CO_2} = 0.37 \pm 0.03$ (standard deviation; 14 values)

Moreover, the data of Bickford et al. leads to 0.35.

Secondly, the authors express their concern about a possible influence of the surface chemistry of the adsorbent on β_{CO_2}. However, as shown in Bickford's Ref. [16], and supported by our own data for CO_2 adsorption on carbons [2], as well as zeolites [3] and MCM-41 [4], the surface chemistry does not affect β_{CO_2}. (Obviously, this is not the case for other adsorptives such as water [5], alcohols [2], etc.). Some authors use β_{CO_2} taken from the literature, which cannot be considered as separate evidence in the present study. Others base their calculations on secondary standards, instead of benzene, which may lead to problems depending on the β values used for these references. In this context, it must be pointed out that in Bickford's Ref. [14] (Cazorla-Amorós et al.), the β_{CO_2} value was *not* taken from the literature, but was calculated so that the characteristic curves for CO_2 and N_2 adsorption coincided. As no activated diffusion was present for N_2, the value $\beta_{CO_2} = 0.35$ may be regarded as a reliable and independent experimental value.

3. Empirical evaluations of β

As pointed out by Dubinin, there exists an empirical correlation between β and the ratio of properties such as parachores, polarizabilities, molar volumes, etc. of the adsorptives (Wood [6]). However, as there exists no theory relating them, their correlation must be regarded as coincidental and treated with care. This means that a prediction based on these ratios may not be used in the assessment of β, itself an experimental quantity (see above). In the present case, this is illustrated by the unrealistic values of β_{CO_2} between 0.53 and 0.69, based on the molar volumes of the free liquid. It is known that the molar volume V_m (CO_2) is be significantly smaller in the adsorbed state, which decreases the expected value of β_{CO_2} accordingly.

References

[1] Bickford ES, Clemons J, Escallón MM, Goins K, Lu Z, Miyawaki J, et al. On the adsorption affinity coefficient of carbon dioxide in microporous carbons. Carbon 2004;42:1867–71.

[2] López-Ramón MV, Stoeckli F, Moreno-Castilla C, Carrasco-Marín F. Specific and non-specific interactions between methanol and ethanol and active carbons. Langmuir 2000;16:5967–72.

[3] García-Martínez J, Cazorla-Amorós D, Linares-Solano A. Further evidences of the usefulness of CO_2 adsorption to characterise micropous solids. Stud Surf Sci Catal 2000;128:485–94.

[4] Berenguer-Murcia A, García-Martínez J, Cazorla-Amorós D, Martínez A, Tascón JMD, Linares-Solano A. About the exclusive mesoporous character of MCM-41. Stud Surf Sci Catal 2002;COPS, 144:83–90.
[5] Stoeckli F. Water adsorption in activated carbons of various degrees of oxidation. Carbon 2002;40:969–71.
[6] Wood GO. Affinity coefficients of the Polanyi/Dubinin adsorption isotherm equations – a review with compilations and correlations. Carbon 2001;39:343–56.

Authors' reply to the above commentary

The readers of CARBON will now have the wherewithal to assess the relative merits of the arguments presented in the two papers; and the path for further research in this area is now clear. The main point of our paper is that the parameter β is hopefully not "only an experimental shifting factor". It is intriguing that Dubinin himself was ambiguous regarding the appropriate terminology: he has used both 'affinity' and 'similarity', the former implicating adsorbate/adsorbent interactions and the latter invoking the properties of the adsorbate only. If β is relegated to a similarity coefficient or an experimental shifting factor, Dubinin's 'theory' is arguably reduced to a convenient statistical distribution function, with no physical significance. There is increasing evidence that gas-phase physisorption phenomena are not the exclusive consequence of non-specific (e.g., dispersion) adsorbate/adsorbent interactions, and that both the surface chemistry and the nature of the adsorbate play an important role in determining the adsorption potential (and thus the affinity of the surface for the adsorbate). If β can somehow reflect these effects, then Dubinin's theory has a bright future, side by side with the already very popular approaches based on density functional theory.