

# Validity of the model used to relate the energy distribution and the adsorption isotherm

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## ABSTRACT

The reproducibility and accuracy of the determination of the adsorption energy distribution for a probe compound on a solid surface is discussed. This distribution can be calculated from the adsorption isotherm, itself derived from the chromatographic profiles of high concentration bands, using the elution by characteristic points method. Distributions derived from experimental data acquired under different experimental conditions agree well within the limits of the reproducibility of these data. Band profiles calculated from the adsorption energy distribution are also in excellent agreement with those recorded.

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## INTRODUCTION

In a separate paper [1], we examined the validity of the model used to derive an equilibrium isotherm from the elution profiles of high-concentration chromatographic bands using the elution by characteristic points (ECP) method. The sources of experimental errors, the accuracy and the precision were discussed. Using comparisons between the experimental elution profiles and the band profiles calculated from the general model of non-linear gas chromatography, we have demonstrated the lack of significant systematic errors.

Adsorption isotherms can be used to understand various aspects of the interactions of the adsorbate molecules with themselves or with the surface of the adsorbent. Currently, we are using the adsorption isotherms of various selected probes to investigate the degree of heterogeneity of a solid surface [2,3]. The adsorption energy distribution of a probe compound on a surface can be calculated by solving a Fredholm integral equation [2]. The complexity of the theoretical problem and of the numerical solution which is needed makes all the more desirable a systematic investigation of the accuracy and repro-

ducibility of the energy distribution derived from the determination of the adsorption isotherm using the ECP method.

We discuss here the problems associated with the derivation of the energy distribution of diethyl ether on the surface of the fine, solid particles used as raw material for the preparation of alumina ceramics [4]. Systematic results obtained with various samples of alumina are reported separately [3].

## THEORY

The apparent or observed adsorption isotherm,  $q(P)$ , is related to the local isotherm,  $\Theta(E,P)$ , and the energy distribution,  $f(E)$ , by the linear, first-kind Fredholm equation [5]:

$$q(P) = \int_{\Omega} \Theta(E,P) f(E) dE \quad (1)$$

where  $E$  is the adsorption energy,  $\Omega$  the energy range considered,  $f(E)$  the fraction of the surface on which the adsorption energy of the probe is between  $E$  and  $E + dE$  and  $\Theta(E,P)$  the local adsorption isotherm of the probe on the fraction of the surface on which the adsorption energy is between  $E$  and

$E + dE$ . Eqn. 1 has no analytical solution; in fact, it has an infinite number of oscillatory solutions [6], and restrictions must be imposed to obtain a solution which has a physical sense.

We have shown [2] how a robust numerical solution can be obtained, by replacing in a first stage the experimental isotherm by a smooth function:

$$q(P) = \sum_k \frac{a_k P}{1 + b_k P} \quad (2)$$

and deriving the values of the numerical coefficients  $a_k$  and  $b_k$  by fitting the experimental data to eqn. 2. Usually, a bi-Langmuir isotherm equation is sufficient. In some instances [2,3], a tri-Langmuir equation becomes necessary. A numerical procedure using the iterative improvement scheme of Adamson and Ling [7] and an algorithm adapted from House and Jaycock [8] has been developed. This procedure usually reveals a multi-modal energy distribution. The minimization of the distance between the experimental isotherm and the isotherm calculated by integration of eqn. 1 is improved in a second stage of optimization in which the experimental isotherm is used and each mode of the energy distribution is represented by a Gaussian distribution if the mode appears symmetrical, by an exponentially modified Gaussian if it is moderately unsymmetrical and by a gamma function if it is strongly unsymmetrical [2]. A simplex routine [9] is used as explained by Adamson and Ling [7]. Convergence is rapid and the method is robust.

Assuming that the exact adsorption isotherm has been determined, four fundamental assumptions made during the derivation of the model of adsorption energy distribution must be discussed and have to be validated for each new application. These assumptions are: (i) the portion of the adsorption isotherm which has been determined experimentally represents accurately the entire sub-monolayer isotherm; (ii) the Langmuir constant,  $K$ , serves to define adequately the thermodynamic reference point; (iii) the intermolecular attractive forces between adsorbate molecules are negligible; and (iv) the adsorbed phase is not mobile (*i.e.*, mass transfer occurs only between the adsorbed phase and the gas phase, not from sites to sites in the adsorbed phase).

The degree of validity of these assumptions may best be assessed by a qualitative description of the

phenomena which take place when adsorption occurs at increasingly high concentrations on heterogeneous surface. The adsorbate molecules do not form a simple, regular monolayer on the surface. High-energy sites are covered first, and local multi-layer coverage of these sites may even take place before total monolayer coverage of the surface occurs [10]. The model of heterogeneous surface we have developed allows for the fact that adsorption is more likely to occur on high-energy than on low-energy sites and that, accordingly, a higher fraction of these sites are covered at any value of the coverage ratio [2]. However, our model does not allow for the possibility of local multi-layer coverage. On the one hand, our model implies that capillary condensation occurs at the point of monolayer capacity, but on the other it fails to take into account any positive (*i.e.*, convex downward) isotherm curvature in the region just below the monolayer capacity. Hence the model implies a discontinuity in the isotherm at the point of monolayer capacity. Clearly, this implication of the assumptions listed above is not realistic and these assumptions are not valid. It can be shown, however, that the error they induce is not significant.

We discuss here the precision and accuracy of the energy distribution obtained following our procedure. The precision was studied by determining the influence of the fluctuations of the experimental conditions on the distance between the energy distributions calculated [1]. The accuracy was studied by comparing the experimental isotherm with the isotherm calculated as a direct solution of eqn. 1.

## EXPERIMENTAL

We have described previously [4] the experimental procedures followed. A quartz open-tubular column (15 m  $\times$  0.53 mm I.D.) was filled with a thin slurry of the particles suspended in a solvent where these particles settle very slowly. After closing one of its ends, the column was coiled inside an oven, through a long, heated metal tube. The solvent vaporized into the oven and was vented, while a thin layer of particles coated the inside wall of the column. The column was then fixed to a Perkin-Elmer (Norwalk, CT, USA) Model 8500 gas chromatograph with a flame ionization detector. After thermal conditioning, large-size samples of the probes

used were introduced into the column and the elution band was recorded. The detector signal was digitized and collected as a computer file. It was transformed into a partial pressure *versus* time elution profile using the detector response factor. The equilibrium isotherm was determined from this profile, using the ECP method [11].

The material studied was RCHP alumina, a high-purity grade of  $\alpha$ -alumina for ceramics manufactured by Malakoff Industries (Malakoff, TX, USA). The dry-ball-milled powder particles had an average diameter of 0.5–0.8  $\mu\text{m}$  and a specific surface area of 8–10  $\text{m}^2 \text{g}^{-1}$ , for a geometrical surface area of *ca.* 1.5  $\text{m}^2 \text{g}^{-1}$ .

## RESULTS AND DISCUSSION

First, as the BET equation does take into account the upward curvature of the isotherm at monolayer capacity, it is instructive to compare the BET surface area with the surface area derived from our model. The total monolayer capacity determined for diethyl ether on RCHP alumina [1] at 60°C was  $7.89 \cdot 10^{-6} \text{ mol g}^{-1}$ . Based on the adsorption area model proposed by Jovanovic [12], and on an assumed molecular diameter of 4 Å for diethyl ether, we calculated the surface area occupied by one molecule of adsorbed diethyl ether to be  $25 \cdot 10^{-20} \text{ m}^2$ . Hence the specific surface area of the alumina sample should be 1.2  $\text{m}^2 \text{g}^{-1}$ . The BET surface area measured for this sample was 8–10  $\text{m}^2 \text{g}^{-1}$ , *i.e.*, 7–8 times larger. It is difficult to expect a better agreement because of the approximations made, including the estimate of the surface area occupied by a molecule of adsorbed diethyl ether, and because as all surfaces have a fractal dimension their specific surface area decrease with increasing molecular size of the adsorbate.

Second, one should consider the self-consistent agreement between the adsorption isotherm derived from the recorded band profiles, using the ECP method, and the isotherm calculated from the energy distribution, as explained above and in ref. 2. This agreement parallels that observed between the profiles recorded during the experiments and those calculated with the semi-ideal model of chromatography, from the isotherm measured by ECP [1]. It shows that the complex calculation procedure is consistent and does converge toward the solution of

eqn. 1. In a previous paper, and in agreement with previous results [13], we have shown that the width of the injection profile had no effect on the simulated chromatogram, as long as it was sufficiently narrow. Nevertheless, calculations were made using the narrowest possible injection. The use of a highly concentrated injection maximizes the influence of the high-surface-coverage portion of the isotherm on the calculated band profile. Hence the magnitude of the error which would be induced by a disagreement between the model and reality is reflected by the magnitude of the error between the calculated and the experimental band profiles.

An example of the degree of agreement obtained between experimental and calculated band profiles is shown in Fig. 1. Application of the retention data difference program [1] to compute the difference parameters for the two bands yields:  $t_{\text{RMS}} = 1.1\%$  and  $\Delta = 8.8 \cdot 10^{-5}$ , where  $t_{\text{RMS}}$  is a measure of the repro-

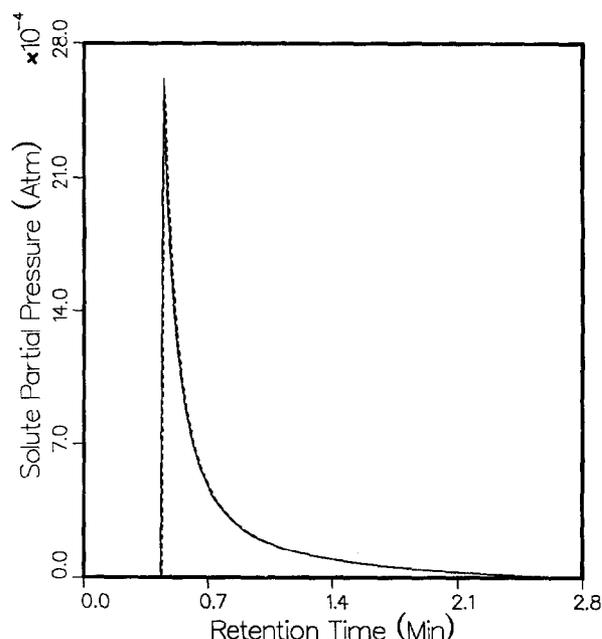


Fig. 1. Comparison between (solid line) the experimental profile obtained for a high-concentration band and (dashed line) the profile calculated from the adsorption isotherm. Diethyl ether on RCHP alumina at 60°C. Experimental conditions: column dimensions, 15 m  $\times$  0.53 mm I.D.; mass of alumina, 44 mg; carrier gas, helium; column inlet pressure, 1.34 atm; outlet pressure, 1.0 atm; column efficiency, 8000 theoretical plate; sample size, 0.45  $\mu\text{g}$ .

TABLE I  
CHANGE IN THE ELUTION BAND PROFILE AS A  
FUNCTION OF THE SAMPLE SIZE

Sample size ( $\mu\text{g}$ )	Peak area (V min)	Shape difference Parameter, $\Delta \times 10^3$
0.50	1.0	2.4
1.0	2.0	6.0
1.5	3.0	12.0
2.5	5.0	31.2
5.0	10.0	121
10.0	20.0	481
15.0	30.0	1080
25.0	50.0	3010

ducibility of the retention time profile [1] and  $\Delta$  is the distance between these two profiles [1]. Both of these difference parameters are much smaller than the corresponding confidence limits for the reproducibility of experimental data acquired the same day and with the same column. This result indicates that the extrapolation of the measured isotherm, and the failure of the model to take into account the possible upward curvature of the isotherm at high

concentrations, cause an error which is smaller than the experimental uncertainty.

As a test of the model which relates the adsorption isotherm and the adsorption energy distribution, further calculations were performed using data regarding the adsorption of diethyl ether on RCHP alumina obtained at column temperatures of 60 and 72°C. Ideally, the adsorption energy distribution and the thermodynamic parameters derived from this distribution should be identical whether they are derived from the isotherms determined at one or the other temperatures. The data were obtained with the same column on different days, and only small differences, which were not statistically significant, were observed. The results are summarized in Table II. The elution profiles recorded at the two temperatures are compared in Fig. 2, the adsorption isotherms in Fig. 3 and the resulting adsorption energy distributions in Fig. 4.

As expected, the retention time is lower at the higher temperature and the tail much shorter. The higher temperature isotherm has a smaller initial slope, but nearly the same saturation capacity. The differences between the thermodynamic parameters

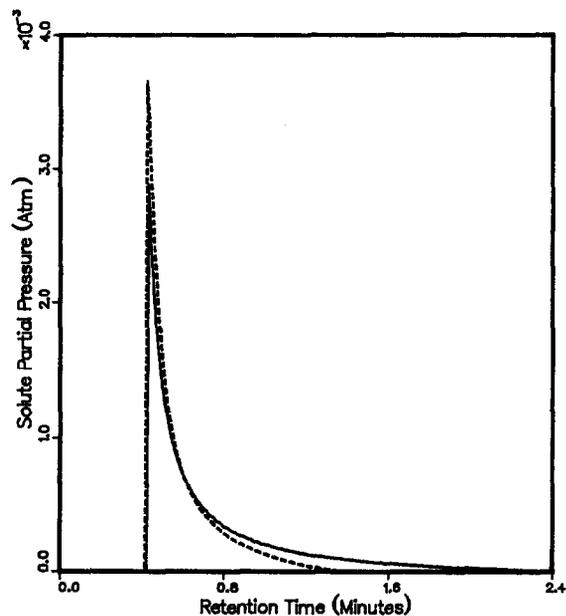


Fig. 2. Elution band profiles of diethyl ether recorded on RCHP alumina at two different temperatures. Experimental conditions as in Fig. 1. Solid line: column temperature, 60°C; peak area, 0.911 V min;  $t_0$ , 22.7 s. Dashed line: column temperature, 72°C; peak area, 0.883 V min;  $t_0$ , 23.0 s.

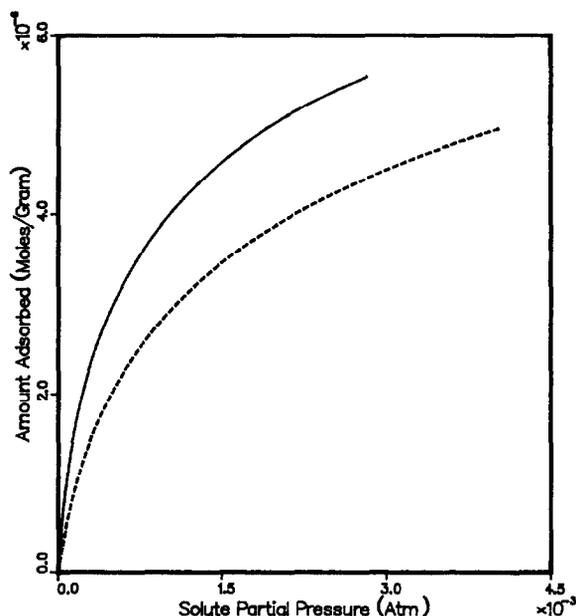


Fig. 3. Adsorption isotherms of diethyl ether on RCHP alumina derived from the band profiles recorded at two different temperatures (profiles in Fig. 2). Solid line, 60°C; dashed line, 72°C.

TABLE II  
CHARACTERISTICS OF THE ADSORPTION ENERGY DISTRIBUTION AT TWO DIFFERENT TEMPERATURES

Parameter <sup>a</sup>	60°C	72°C	Relative difference (%)
$q_{s,1}$ ( $\mu\text{mol g}^{-1}$ )	5.36	5.2	-3.0
$E_{\text{AVG},1}$ ( $\text{kcal mol}^{-1}$ )	11.04	10.9	-1.0
$\sigma_1^2$	17	11	-34
$q_{s,2}$ ( $\mu\text{mol g}^{-1}$ )	2.53	92.64	4.3
$E_{\text{AVG},2}$ ( $\text{kcal mol}^{-1}$ )	12.68	12.54	-1.0
$\sigma_2^2$	1.0	1.0	2.3

<sup>a</sup>  $q_{s,1}$ ,  $q_{s,2}$ : specific saturation capacity of the two modes of the adsorption energy distribution.

$E_{\text{AVG},1}$ ,  $E_{\text{AVG},2}$ : average energy of the two modes of the adsorption energy distribution.

$\sigma_1^2$ ,  $\sigma_2^2$ : variance of the two modes of the adsorption energy distribution; in  $10^{-6} \text{ kcal}^2 \text{ mol}^{-2}$ .

calculated from the two adsorption energy distributions are smaller than the differences expected for parameters derived from experimental data ob-

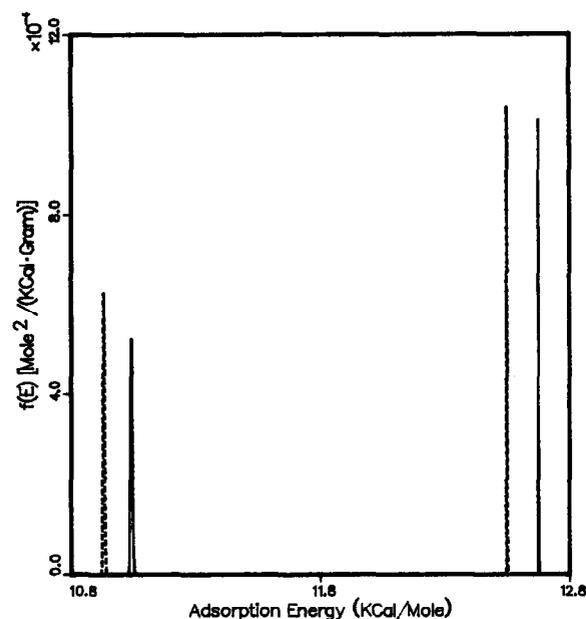


Fig. 4. Adsorption energy distribution of diethyl ether on RCHP alumina determined at two different temperatures (isotherms in Fig. 3). Solid line, 60°C; dashed line, 72°C.

tained with the same column on different days (see Table II). The fact that there are two modes in Fig. 4 is not a consequence of the use of a bi-Langmuir isotherm during the first stage of the calculation procedure. This isotherm is used to enable the numerical solution of a less ill-condition problem [2]. Details of the procedure used to determine which analytical isotherm should be used in the first stage of a particular optimization have been presented [3]. The experimental isotherm is used in the second stage of the optimization, so the number of modes is not an artefact of the calculation procedure. Trimodal energy distributions have been measured with some samples [3].

Finally, earlier studies [6,14,15] have compared the results of the calculations of adsorption energy distributions made using the Langmuir model of localized adsorption with the results of more sophisticated models which take into account intermolecular interactions between sorbed molecules and/or the mobility of the adsorbed phase on the solid surface. These studies have shown that the only difference is a constant shift in energy for the entire distribution.

There are several good reasons for using a simple model of adsorption energy distribution, as we did. First, the aim of the whole study is to compare different adsorbates. For this purpose, it does not really matter what thermodynamic reference point is used, as long as the series of results are self-consistent [3]. Second, a more sophisticated model may increase the complexity of the problem, and especially of its numerical analysis, to a point of intractability. Finally, a thermodynamic reference point which is based on physically measurable quantities (*i.e.*, on the physicochemical properties of the solute) is more desirable than a thermodynamic reference point which is based either on some property of the isotherm, which is subject to experimental error, or on factors which have to be calculated through quantum mechanics and which depend on assumptions which are difficult to prove or validate.

## CONCLUSIONS

This work shows that highly reproducible data regarding the adsorption energy distribution of probes on solid surfaces can be derived from chromatographic data which are easy to obtain using

conventional, commercial equipment and simple experimental procedures. These data are also self-consistent, as the band profiles can be calculated from adsorption isotherms which, in turn, can be derived from the adsorption energy distribution.

The features of the adsorption energy distribution, such as the mean energy of a mode of this distribution, may, to some extent, be relative and not absolute quantities. This mean adsorption energy may be shifted with respect to the value derived from the conventional thermodynamic reference point. Nevertheless, these data are extremely useful as they permit an easy and detailed characterization of solid surfaces [3].

This work has demonstrated the potential usefulness of the systematic determination of adsorption energy distribution for series of selected probes in order to characterize solid surfaces and investigate material properties which are related to the chemistry of the gas-solid surface.

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