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A New Method for the Prediction of Adsorption Isotherms

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ABSTRACT

A universally applicable method of predicting the isotherms of pure gas physical adsorption equilibrium is proposed. This makes it possible to predict the equilibrium amount of adsorption using only the thermodynamic parameters of adsorbate gases, i.e. T_c, P_c, T_{nbp} *and* ω. *This method is based on four assumptions related to the properties of the adsorption system, namely:*

1. *The adsorbed phase consists of two phases, i.e. a 'pseudo-liquid' phase and a 'pseudo-vapour' phase.*
2. *An adsorbent has a maximum available adsorption space,* ϕ_{max}.
3. *The density of the adsorbed at the surface of adsorbent,* ρ_0, *can be expressed as:*

$$\rho_0 = C_1\left(\frac{T_c}{T}\right)C_2\left(\frac{P}{P_c}\right)C_{3\omega}C_4$$

where, C_1, C_2, C_3 *and* C_4 *are constants whose values depend on the characteristics of the adsorbent and* T_c, P_c, T_{nbp} *and* ω *are the critical temperature, critical pressure, normal boiling temperature and Pitzer's acentric factor, respectively.* T *and* P *are the temperature and the pressure at adsorption equilibrium, respectively.*

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(4) The volume of the 'pseudo-liquid' phase can be expressed as:

$$\phi_s = d_1\left(\frac{T_c}{T}\right)d_2\left(\frac{P}{P_c}\right)d_{3\omega}d_4$$

where, d_1, d_2, d_3 and d_4 are constants whose values are dependent on the characteristics of the adsorbent, while T_c, P_c, T_{nbp} and ω have the same meaning as above.

The equilibrium amount of adsorption predicted using the proposed method has been compared with experimental values. An average deviation of 9·3% between the two approaches is seen. The correlation equation obtained by analysis of data acquired for an individual adsorption system applies to other systems based on the same adsorbent coupled with a different adsorbate gas. An attractive feature of the proposed method is that prediction of adsorption isotherms using the proposed method only requires information relating to the thermodynamic properties of the adsorbate, i.e. T_c, P_c, T_{nbp} and ω.

NOTATION

a, b	Coefficients in reciprocal function
A	Total amount of adsorption
$A_{expt.}$	Total amount of adsorption obtained by experiment
$A_{pred.}$	Total amount of adsorption obtained by prediction
C_1, C_2, C_3, C_4	Characteristic parameters of adsorbent relating to the density of adsorbed phase on the surface of adsorbent
d_1, d_2, d_3, d_4	Characteristic parameters of adsorbent relating to the volume of 'pseudo-liquid' phase
E	Minimum of objective function for optimisation
T, P	Temperature and pressure at the adsorption equilibrium
T_c, P_c	Critical temperature and pressure
T_{nbp}	Normal boiling point
$\theta, \theta_C, \theta_d$	Objective functions for optimisation
ρ_g	Density of adsorbate at gaseous state
ρ_l	Density of adsorbate at liquid state
ρ_{sl}	Density of 'pseudo-liquid' phase
ρ_{sv}	Density of 'pseudo-vapour' phase
ρ_v	Density of adsorbate at vapourous state
ρ_0	Density of adsorbed phase on the surface of adsorbent
σ, K	Coefficients in Gaussian distribution function
ϕ	Volume of adsorbed phase
ϕ_{max}	Volume of maximum available adsorption space
ϕ_s	Volume of 'pseudo-liquid' phase
ω	Pitzer's acentric factor

1 INTRODUCTION

Evaluation of adsorption isotherms can be classified into statistical thermodynamic evaluations, kinetic evaluations and two-dimensional condensation thermodynamic evaluations (surface pressure or adsorption potentials). The isotherm models thus evaluated can be classified into two sub-groups. One of these is based on the Langmuir theory and is characterised by its successful explanation of microkinetic equilibria in the adsorption system. From the physical point of view, this group of models can satisfactorily describe the microprocess which operates during the adsorption. These descriptions are well supported by molecular kinetics. Also, all of these models give straightforward adsorption isotherms. Research to date, associated with these models, has shown that the models can be used to correlate various types of adsorption isotherms. However, one disadvantage of these models is that they contain no coefficient which reflects the characteristics of the adsorbent and of the adsorbates. Therefore, the coefficients obtained through approximation of adsorption isotherms at an individual temperature cannot be used to predict the adsorption isotherms at other temperatures. Predictions of an adsorption isotherm based on these models involve interpolation or extrapolation of the adsorption isotherm at specified temperature, using models obtained by correlation of the experimental adsorption isothermal data at the same temperature. In other words, these models have very limited application in practice, with respect to being able to predict equilibrium adsorption data, though they can be used successfully to correlate isothermic adsorption data. Wheeler (in Ref. 1) pointed out that the development of these models concerns the further study of the interactive energy (a) between adsorbate molecules and (b) between adsorbate molecules and adsorbent molecules. However, such considerations bring about further difficulties. This is because they involve assumptions about the adsorption system, which in turn produce mathematical complexities that cannot be satisfactorily rationalised by existing mathematical approaches.

Another group of adsorption models is based on the adsorption potential theory first proposed by Polanyi.[2,3] These models emphasise the macromolecular kinetic characteristics of adsorption systems rather than the micromolecular kinetic aspects. These models describe the equilibrium between the adsorbate and adsorbent as being gas-liquid equilibrium in type, and do not give explicit adsorption isotherms. Instead, the adsorption isotherms can be obtained by calculation, based on the adsorption characteristic curves. One outstanding feature of these models is that the adsorption characteristic curves are not temperature dependent. Therefore, isotherms at various adsorption temperatures can be obtained based on one adsorption characteristic curve. It should be emphasised here that one of the great advantages of adsorption potential models is that to obtain the adsorption characteristic curve, no details of intermolecular energies or of the distribution of the intermolecular energy are required. This advantage is emphasised because one tempting option in modifying these models, which is not a suitable approach in the authors' opinion, is to introduce more molecular kinetic parameters with the intention of achieving greater precision. This is because such an operation would eliminate the advantage of the adsorption potential theory and could bring mathematical difficulties into the models. Therefore, a more meaningful modification of the existing adsorption potential models should be aimed at the establishment of a model which has universal applicability to various adsorption systems rather than at the provisions of improvement designed to achieve a higher degree of approximation. A number of modifications towards achieving universal applicability of adsorption potential models have been published.[1,4-10] The most noteworthy modification was that made by Dubinlin.[4] However, there is still no unique model which is capable of describing all adsorption equilibria of different adsorbates on the same adsorbent. The universal applicability of adsorption isotherm model is of vital importance to many 'real' systems such as the application of disperse dyes on fabrics, the purification of gaseous effluent streams and various catalytic processes, separation processes by chromatographic techniques and characterisation procedures related to inverse gas chromatography. Here, the authors wish to establish the procedures/principles upon which the model is based.

2 THE PROPOSED ADSORPTION EQUILIBRIUM MODEL

2.1 The model

The adsorption picture described in this paper is adapted from Polanyi's adsorption potential theory. In order to facilitate easier understanding of the authors' modifications, the density distribution curve associated with the adsorbate have been employed, as first proposed by Lowry and Olmstead.[11] This approach is shown diagrammatically as Fig. 1.

In Fig. 1, ρ represents the density of the adsorbed phase and ϕ the volume of the adsorbed phase. The maximum density of the adsorbed phase (denoted as ρ_{max}) is greatest at the surface of the adsorbent and least at the interface between the gaseous phase and the adsorbed phase (denoted as ρ_g). The shape of the density distribution curve is, to a large extent, dependent on the temperature and pressure at which the adsorption process occurs. Curves 1–3 are relevant to three different cases of adsorption. Curve 1 describes the adsorption system when the adsorption temperature is far

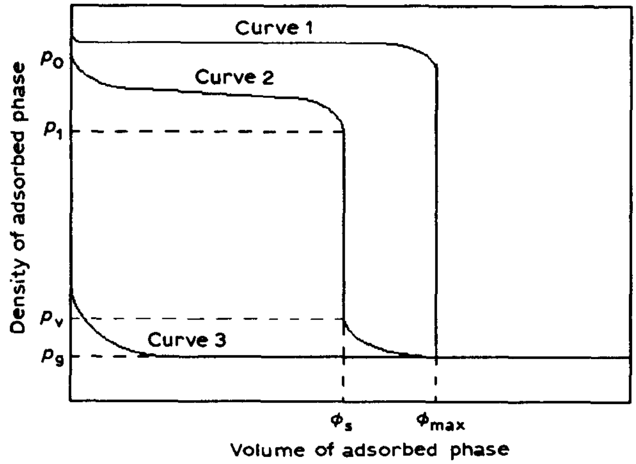

Fig. 1. Density distribution of adsorbed phase.

lower than the critical temperature of the adsorbate gas and the adsorption pressure is close to the saturation vapour pressure of the adsorbate gas. In this case, the whole adsorption space is filled with liquidised adsorbate. Curve 3 describes the adsorption system where the adsorption temperature is much higher than the critical temperature, and thus the whole adsorption space is occupied by compressed adsorbate gas. Curve 2 is relevant to an intermediate case where part of the adsorbate space, 0–ϕ_s, is filled with the liquidised adsorbate and the rest of the adsorbate space, ϕ_s–ϕ_{max}, is occupied by compressed adsorbate gas. One feature of the adsorbed phase which should be noted is that, although the volume of the phase represented as ϕ_s–$\phi_{max}$is larger than that of the phase 0–ϕ_s, the value of total adsorbate is mainly made up by the phase 0–ϕ_s because the density of this phase is much higher than that of phase ϕ_s–ϕ_{max}.

From Fig. 1, we can see that the total adsorbate can be expressed by eqn (1):

$$A = \int_0^{\phi_{max}} \rho \, d\phi - \rho_g \phi_{max} \tag{1}$$

where A denotes the total amount of adsorption. In most cases, $\rho_g \phi_{max}$ is negligible. Therefore, the total adsorbate can be obtained by integration of $\rho \, d\phi$ between 0 and ϕ_{max}. Thus, we have:

$$A = \int_0^{\phi_{max}} \rho \, d\phi \tag{2}$$

$$A = \int_0^{\phi_s} \rho_l \, d\phi + \int_{\phi_s}^{\phi_{max}} \rho_v \, d\phi \tag{3}$$

Therefore, to obtain the amount of adsorption, four parameters must be fixed. These are the volumes of two adsorbed phases, ϕ_s and ϕ_{max}, and the density distribution function of these two phases, i.e. $\rho_l = f_l(\phi)$, $\phi = [0, \phi_s]$ and $\rho_v = f_v(\phi)$, $\phi = [\phi_s, \phi_{max}]$. Lowry and Olmstead[11] did not give the functional relationship between the density of adsorbate ρ and the volume of the adsorbate ϕ, i.e.:

$$\rho = f(\phi) \tag{4}$$

In fact, no results have been published which are relevant to the evaluation of this functional relationship. The rest of this paper deals with the evaluation of these values by introducing four assumptions. These assumptions are based on the conclusion obtained through analysis of a large array of adsorption data from various adsorption systems. The reliability of these assumptions was tested by the adsorption data obtained from studies of the adsorption of nitrogen and of methane on Linde molecular sieves MS-13X.[12]

2.1.1 *Hypothesis 1*

In the adsorption system visualised, the adsorbate is composed of two phases. The first phase has a volume of ϕ_s and occupies the adsorbed phase space from 0 to ϕ_s. The density of the adsorbate in this phase is higher than that of the same adsorbate in the liquid state. For convenience, we shall call this phase the 'pseudo-liquid' phase. The density distribution in this phase, i.e. the functional relationship between the density of 'pseudo-liquid' phase, denoted as ρ_{sl}, and ϕ can be approximated by a Gaussian function. The second phase has the volume of $(\phi_{max} - \phi_s)$ and occupies the adsorbed phase space from ϕ_s to ϕ_{max}. The density of this phase, denoted as ρ_{sv}, is higher than the density of the same adsorbate in the gaseous state at the same temperature and pressure, but lower than the vapour density of the same adsorbate. For convenience, in later discussion we shall refer to this phase as the 'pseudo-vapour' phase. Therefore, we have $\rho_{vapour} > \rho_{sv} > \rho_g$. The density distribution of this phase can be represented by reciprocal function. There is an interface between the 'pseudo-liquid' and 'pseudo-vapour' phases. The continuity of the density distribution of the adsorbed phase breaks at this interface. 'Pseudo-liquid' and 'pseudo-vapour' phases are always in a state of equilibrium which can be described through the equations of state. The density distribution of the adsorbate phase according to this hypothesis is given as Fig. 2.

Although the selection of Gaussian and reciprocal functions to represent the density distribution of 'pseudo-liquid' and 'pseudo-vapour' phases are based on mathematical resemblance between these mathematical functions and the density distribution curves, a close look at the density distribution curves in Fig. 2 will reveal that these two functions give rational continuity of density distributions in the entire adsorption space.

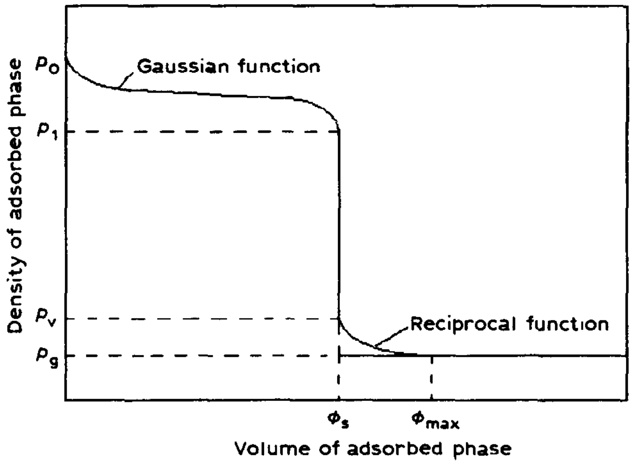

Fig. 2. Mathematical functions simulating the density distribution of the adsorbed phase.

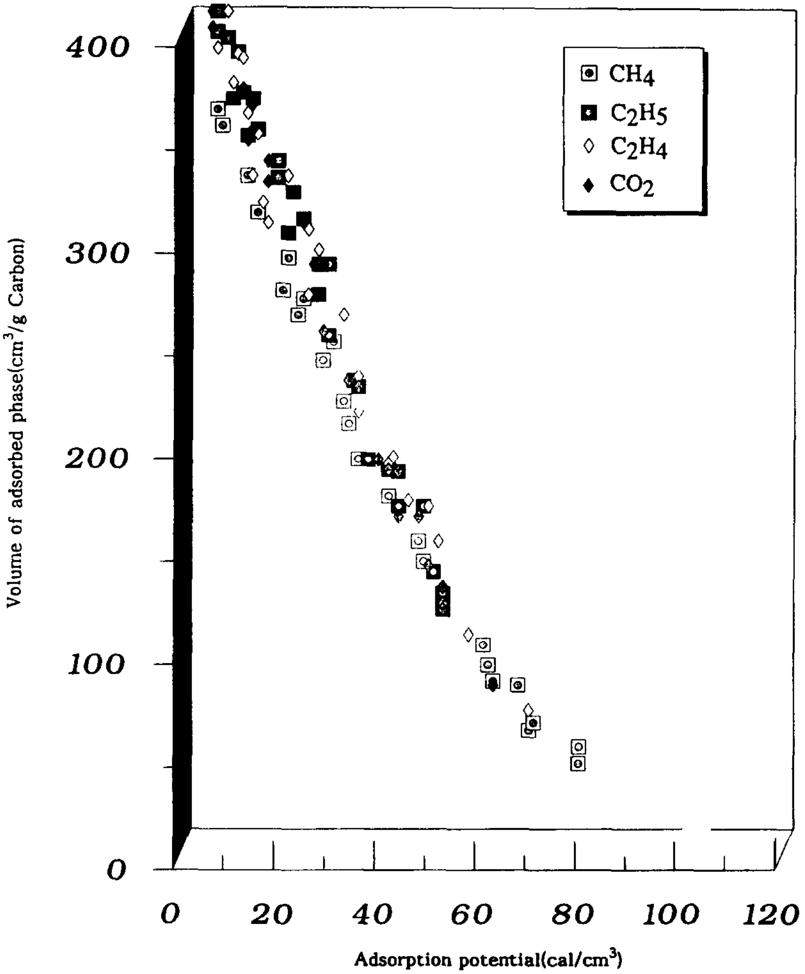

Fig. 3. Characteristic curve for pure gases, $T = 212{\cdot}7$–$301{\cdot}4$ K.

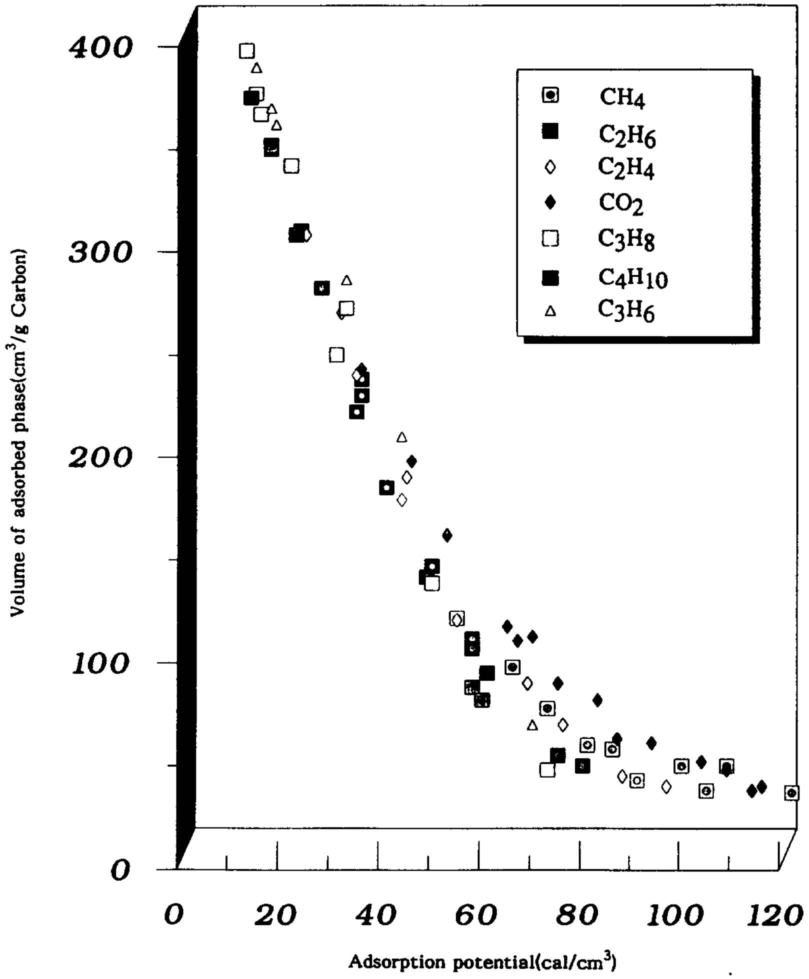

Fig. 4. Characteristic curve for gas mixtures, $T = 212{\cdot}7\text{–}301{\cdot}4$ K.

2.1.2 *Hypothesis 2*

An adsorbent has a maximum available adsorption space, $\phi_{\max}$, which is dependent only on the properties of the adsorbent. $\phi_{\max}$ is close in value to the pore volume of adsorbent. This is clear if we examine the adsorption data of methane, ethane, ethylene, carbon dioxide, etc., on BPL activated carbon (Pittsburg Chemical Co. Inc., Pittsburg, USA) as shown in Figs 3–5.[13]

2.1.3 *Hypothesis 3*

In the adsorption system, the density of the adsorbate phase at the surface of adsorbent, ρ_0, is dependent on the thermodynamic properties of the adsorbent, the adsorbate and on the adsorption equilibrium temperature

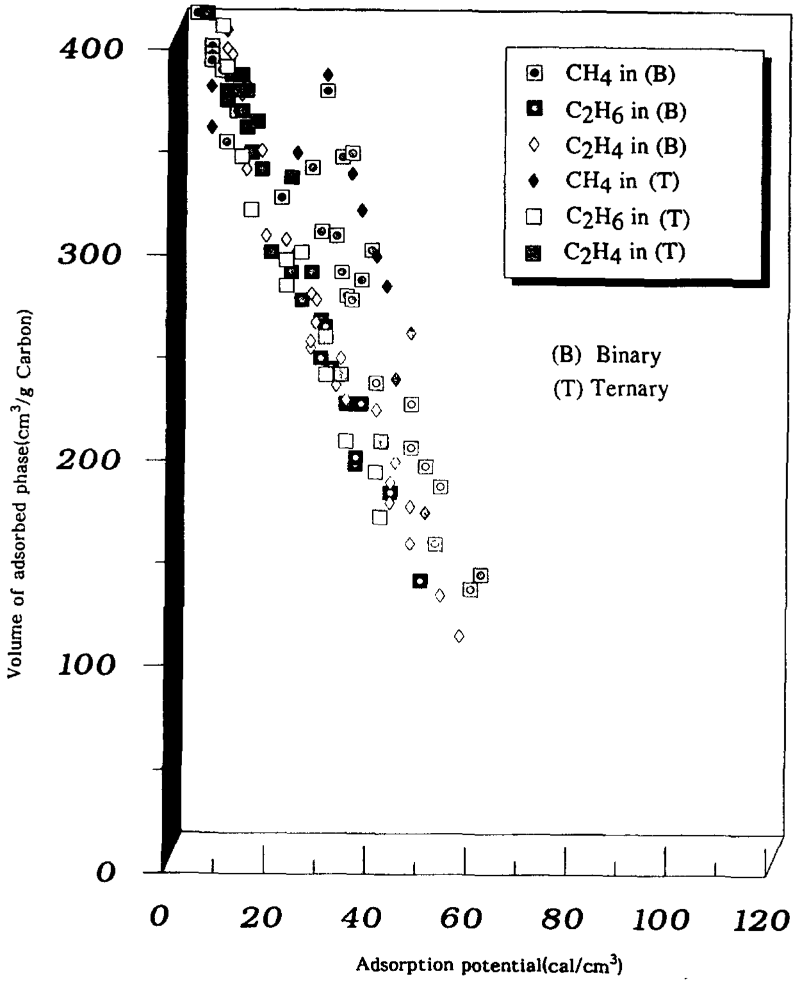

Fig. 5. Characteristic curve for pure gases at 293 and 363 K.

and pressure. This is represented as eqn (5):

$$\rho_0 = \mathscr{F}(\text{characteristics of adsorbent}, T, P, T_c, P_c, \omega) \qquad (5)$$

where T and P denote the adsorption temperature and pressure, and T_c, P_c and ω have the same meanings as previously. We assume that this equation can be further modified to give eqn (6):

$$\rho_0 = C_1\left(\frac{T_c}{T}\right)C_2\left(\frac{P}{P_c}\right)C_{3\omega}C_4 \qquad (6)$$

where C_1, C_2, C_3 and C_4 are constants with their values dependent only on the characteristics of the adsorbent. In other words, we assume that the influence of the properties of the adsorbent on ρ_0 can be represented by the four coefficients, C_1, C_2, C_3 and C_4, and those of adsorbate gas by T_c, P_c and ω. The values of coefficients C_1, C_2, C_3 and C_4 should be the same for adsorption equilibrium systems consisting of the same adsorbent but different adsorbates.

2.1.4 Hypothesis 4

In adsorption equilibrium systems, the volume of the adsorbate space occupied by the 'pseudo-liquid' phase, ϕ_s, is dependent on the characteristics of the adsorbent, the thermodynamic properties of the adsorbate and the temperature and pressure of the environment. This implies that the following equation exists:

$$\phi_s = \mathscr{G}\,(\text{characteristics of adsorbent}, T, P, T_c, P_c, \omega) \tag{7}$$

This equation is further modified to give:

$$\phi_s = d_1\left(\frac{T_c}{T}\right)d_2\left(\frac{P}{P_c}\right)d_{3\omega}d_4 \tag{8}$$

where d_1, d_2, d_3 and d_4 are constants with their values dependent only on the characteristics of the adsorbent. T_c, P_c, ω, T, and P have the same meanings as given earlier. In other words, the coefficients d_1, d_2, d_3 and d_4, obtained from one adsorption equilibrium system, can be used to predict ϕ_s of other adsorption equilibrium systems based on the same adsorbent.

2.2 Deduction of density distribution functions of the adsorbed phase

As stated above, the adsorbate phase can be assumed to consist of two phases, i.e. the 'pseudo-liquid' and the 'pseudo-vapour' phases. The authors also hypothesise that the density distribution functions can be described by Gaussian functions for the 'pseudo-liquid' phase and by a reciprocal function for the 'pseudo-vapour' phase. To deduce the terms of these density distribution functions, we need to examine the Gaussian function and reciprocal function which represent the density distributions. First, the density distribution functions were constructed by comparing the density distribution curves in Fig. 2 with Gaussian function and reciprocal function approaches.

For the 'pseudo-liquid' phase, we have:

$$\phi(\rho) = \frac{1}{2\pi\sigma}\exp\left[-\frac{(\rho-\rho_{sl})^2}{2\sigma^2}\right] \tag{9}$$

when $\rho_0 > \rho > \rho_{sl}$.

However, eqn (9) cannot simultaneously satisfy the boundary conditions, that:

$$\text{when } \rho = \rho_{sl} \qquad \phi(\rho) = \phi_s \tag{10}$$

and

$$\text{when } \rho = \rho_0 \qquad \phi(\rho) = 0 \tag{11}$$

Therefore, eqn (9) is further modified by involving a coefficient$K$. This leads to eqn (12):

$$\phi(\rho) = \frac{K}{2\pi\sigma} \exp\left[-\frac{(\rho - \rho_{sl})^2}{2\sigma^2} \right] \qquad \text{when } \rho_0 > \rho > \rho_{sl} \tag{12}$$

From eqn (12), $\phi(\rho) = 0$ is true only when ρ approaches infinity. Therefore, boundary conditions (11) must be further modified to give physical rationality. Thus, we have the modified boundary conditions as:

$$\text{when } \rho = \rho_{sl} \qquad \phi(\rho) = \phi_s \tag{10}$$

$$\text{when } \rho = \rho_0 \qquad \phi(\rho) = 1E - 8 \tag{13}$$

Substituting boundary conditions (10) and (13) into eqn (12) allows us to obtain the density distribution parameters K and σ, expressed as follows:

$$K = 2\pi\sigma\phi_s \tag{14}$$

$$\sigma = \frac{\rho_0 - \rho_{sl}}{2 \ln (\phi_s + 18)} \tag{15}$$

Once ρ_0, ρ_1 and ϕ_s are set, the density distribution of the 'pseudo-liquid' phase is obtainable. The approach to obtaining ρ_0, ρ_1 and ϕ_s for a specific adsorption system will be discussed later.

For the 'pseudo-vapour' phase, we have:

$$\rho_{sv} = a + b/\phi \tag{16}$$

where a and b are distribution parameters. From Fig. 2, we can see that eqn (16) must satisfy the following two boundary conditions:

$$\rho_v = a + b/\phi_s \tag{17}$$

$$\rho_g = a + b/\phi_{max} \tag{18}$$

Rearrangement of these two equations gives the following expressions:

$$a = \frac{\rho_g\phi_{max} - \rho_v\phi_s}{\phi_{max} - \phi_s} \tag{19}$$

$$b = (\rho_v - a)\phi_s \tag{20}$$

2.3 Prediction of adsorption isotherms using the proposed approach

According to the density distribution of the adsorbate phase as given in Fig. 2, the total extent of adsorption can be given as:

$$A = \int_0^{\phi_s} \rho_{sl}(\phi)\, d\phi + \int_{\phi_s}^{\phi_{max}} \rho_{sv}(\phi)\, d\phi - \rho_g\phi_{max} \tag{21}$$

where A represents total amount of adsorption, $\rho_{sl}(\phi)$ denotes the density distribution function of 'pseudo-liquid' phase, $\rho_{sv}(\phi)$ denotes the density distribution function of 'pseudo-vapour' phase and ρ_g denotes the density of the adsorbate gas at the adsorption equilibrium temperature and pressure.

The density distribution function of the 'pseudo-liquid' phase can be deduced from eqns (14) and (15). Thus, we have:

$$\rho_{sl}(\phi) = \rho_l + [-2\ln(2\pi\sigma\phi/K)]^{1/2} \tag{22}$$

$$\sigma = (\rho_v - \rho_l)/[2(18 + \ln\phi_s)] \tag{23}$$

$$K = 2\pi\sigma\phi_s \tag{24}$$

The density distribution function of the 'pseudo-vapour' phase is as follows:

$$\rho_{sv}(\phi) = a + b/\phi \tag{25}$$

$$a = (\rho_g\phi_{max} - \rho_v\phi_s)/(\phi_{max} - \rho_v) \tag{26}$$

$$b = (\rho_g - a)\phi_s \tag{27}$$

Therefore, to predict the amount of adsorption, three important parameters, ϕ_s, ϕ_{max} and ρ_0, are required. Other parameters, i.e. ρ_l, ρ_v, and ρ_g are readily obtainable through the equation of state. To determine the values of parameters ϕ_s, ϕ_{max} and ρ_0, experimental data of one adsorption system must be provided in order to obtain the coefficients C_1, C_2, C_3 and C_4 as outlined in eqn (6), d_1, d_2, d_3 and d_4 in eqn (8) and ϕ_{max}. According to the hypotheses 1–4 in Section 2.1, these parameters are constant for adsorption systems consisting of the same adsorbent and various adsorbate gases. In other words, these coefficients, although constructed through a set of adsorption equilibrium data of a specific adsorption system, remain constant in adsorption comprising the same adsorbent with various adsorbate gas and under various equilibrium temperature and pressure.

Thus, a route for predicting the amount of adsorption is devised. For convenience, we shall deal with the prediction of adsorption isotherms of various adsorbate gases on molecular sieves MS-13X.[12] The route is given below.

2.3.1 Measurement of adsorption isotherm of carbon dioxide on MS-13X

As mentioned above, in order to predict adsorption isotherms of various gases on the same adsorbent, one adsorption isotherm must be provided. The adsorption isotherm of nitrogen on Linde molecular sieves MS-13X at 273·15 K is given in Fig. 6.

2.3.2 Determination of characteristic parameters of adsorbent MS-13X

To evaluate the values of the characteristic parameters of MS-13X, the optimal values of ρ_0, ϕ_s and ϕ_{max} are determined using the adsorption

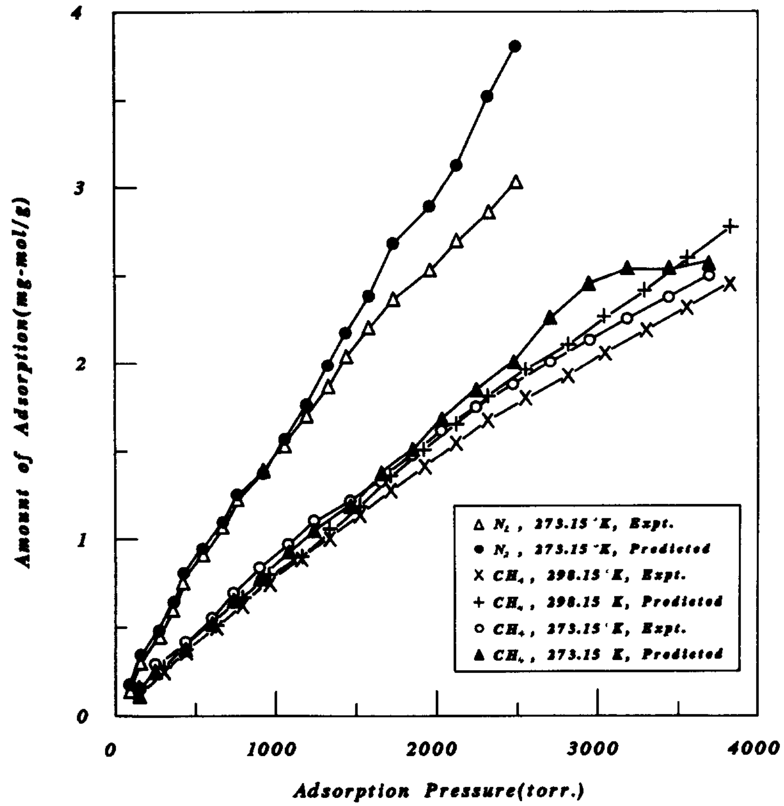

Fig. 6. Adsorption isotherms: experiment data and data predicted by proposed method.

isotherm data. This evaluation procedure is given as Fig. 7. This computation procedure is designed based on the principle of multivariable optimisation. In other words, the values of ρ_0, ϕ_s and ϕ_{max} are obtained by optimising these parameters according to the objective function:

$$\theta = (A_{expt.} - A_{pred.})^2 \qquad (28)$$

In eqn (28), θ denotes the value of the objective function, $A_{expt.}$ denotes the total amount of adsorption obtained by experiment, and $A_{pred.}$ denotes the total amount of adsorption predicted by using eqns (21)–(31).

The purpose of each computation is given in steps (1)–(9) below.

(1) The adsorption temperature T, critical parameters of adsorbate gas T_c and P_c, Pitzer's acentric factor ω, and normal boiling point of adsorbate gas T_{nbp} are required in computation. In the authors' case, i.e. the adsorption equilibrium of nitrogen on MS-13X at 273·15 K, the parameters are $T = 273{\cdot}15$ K, $T_c = 126{\cdot}2$ K, $P_c = 3{\cdot}4E-6$ Pa, $\omega = 0{\cdot}04$ and $T_{nbp} = 77{\cdot}35$ K.

(2) Starting from the first data point, the value of the pressure of

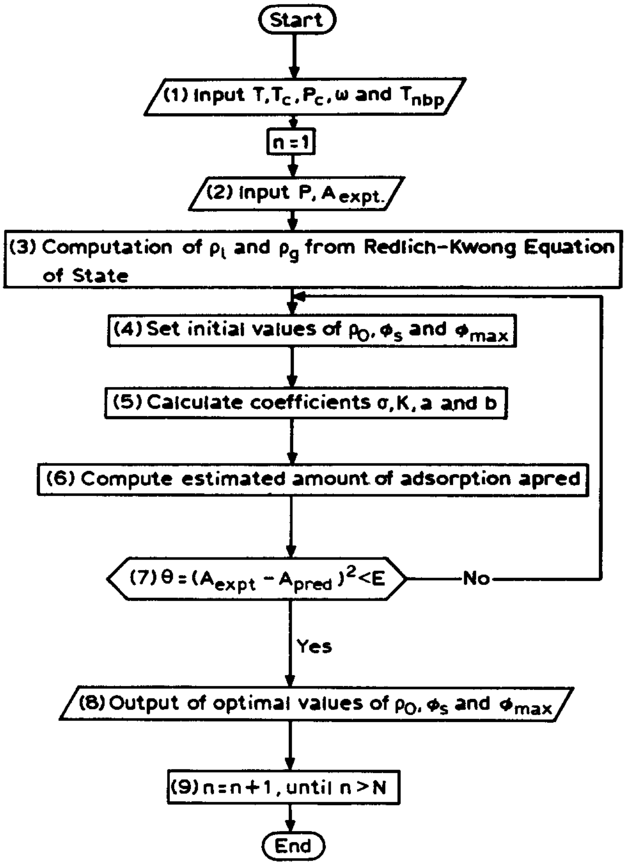

Fig. 7. The computation procedure for evaluation of ρ_0, ϕ_s and ϕ_{max}.

adsorption equilibrium P and the value of the amount of adsorption, $A_{expt.}$ are input as required.

(3) By using an equation of state, the gaseous density of adsorbate, ρ_g and the liquid density of adsorbate ρ_l can be computed using the parameters T, P, T_c, P_c, ω and T_{nbp}. In the present study, the Redlich–Kwong equation of state,[14] shown as eqns (29)–(31), was used:

$$P = \frac{RT}{V-b} - \frac{a}{T^{1/2}V(V+b)} \tag{29}$$

$$a = \frac{0{\cdot}427\,580\,2R^2T_c^{2\cdot5}}{P_c} \tag{30}$$

$$b = \frac{0{\cdot}086\,64RT_c}{P_c} \tag{31}$$

In eqn (29), V denotes the molar volume of the adsorbate.

(4) In order to start the optimisation process, initial values of ρ_0, ϕ_s and ϕ_{max} must be provided. The general principle for setting these initial parameters according to the authors' experience, is to set ρ_0 as $1{\cdot}5\rho_1$, ϕ_s as $0{\cdot}5\phi_{max}$, and ϕ_{max} as the total volume of pores of the relevant adsorbent.

(5) Density distribution parameters of 'pseudo-liquid' and 'pseudo-vapour' phases, i.e. σ, K, a and b, are obtained using eqns (23), (24), (26) and (27).

(6) Estimation of the total amount of adsorption using eqns (21), (22) and (25) is then undertaken.

(7) The end point of optimisation is determined by the value of the objective function given as eqn (28). The minimum of the objective function is set depending on the units used for the amount of adsorption. In most cases, the criterion for setting the values of E, given in eqn (32), is recommended:

$$E < 0{\cdot}01(A_{expt.})_{min} \tag{32}$$

where $(A_{expt.})_{min}$ represents the minimum of the total amount of adsorption obtained through the experiment. If criterion (28) is not satisfied, new values of ρ_0, ϕ_s and ϕ_{max} will be set automatically according to the numerical optimisation programme. The computation will then start from step (3) to step (8). The numerical optimisation algorithm employed in this work is the Powell's Optimisation Algorithm.[15]

(8) The optimisation process operates until the objective criterion, as represented by eqn (28), is satisfied. The values of optimal ρ_0, ϕ_s and ϕ_{max} are thus obtained.

(9) Operations (4)–(7) are repeated for each of the experiment data point.

2.3.3 Evaluation of adsorption characteristic parameters

Upon obtaining a series of values of ρ_0, ϕ_s and ϕ_{max}, computation can be carried out to evaluate the adsorbent characteristic parameters, C_1, C_2, C_3, C_4, d_1, d_2, d_3 and d_4. The Powell's multivariable optimisation technique is again employed. The objective functions are as follows.

For evaluation of C_1, C_2, C_3, and C_4:

$$\theta_C = \sum_{i=1}^{N} [\rho_0 - C_1(T_c/T)C_2(P/P_c)C_{3\omega}C_4]^2 \tag{33}$$

For evaluation of d_1, d_2, d_3 and d_4:

$$\theta_d = \sum_{i=1}^{N} [\phi_s - d_1(T_c/T)d_2(P/P_c)d_{3\omega}d_4]^2 \tag{34}$$

In eqns (33) and (34), N denotes the total number of experimental data points involved in the optimisation. As in the adsorption of nitrogen on MS-13X, the authors obtained, through the computation described above and using the adsorption isotherm data, the characteristic parameters of adsorbent MS-13X as:

$C_1 = 2{\cdot}103$
$C_2 = 1{\cdot}091$
$C_3 = 0{\cdot}873$
$C_4 = 0{\cdot}772$
$d_1 = 2{\cdot}327$
$d_2 = 1{\cdot}281$
$d_3 = 0{\cdot}317$
$d_4 = 0{\cdot}507$
$\phi_{\max} = 0{\cdot}3\ \mathrm{cm}^3/\mathrm{g}$ (this value is very close to the total pore volume of Linde molecular sieves MS-13X, which is 0·32)

2.3.4 *Evaluation of adsorption isotherms*

Knowing the characteristic parameters of the adsorbent, i.e. C_1, C_2, C_3, C_4, d_1, d_2, d_3, d_4, and the volume of maximum adsorption space, $\phi_{\max}$, adsorption isotherms of adsorption of various adsorbate gases on the same adsorbent, at various temperatures, can be predicted according to the following procedures (Fig. 8). Each of the procedures in Fig. 8 is detailed as follows:

(1) First, the values of the critical temperature T_c, critical pressure P_c, Pitzer's acentric factor ω, and normal boiling T_{nbp} of the adsorbate are input. Also required are the characteristic parameters of the relevant adsorbent, i.e. C_1, C_2, C_3, C_4, d_1, d_2, d_3, d_4 and $\phi_{\max}$
(2) The temperature of adsorption, at which the isotherm of adsorption is sought, is specified.
(3) The range of pressures of the intended prediction is specified.
(4) The value of pressure is established at a low point and the density of adsorbate at liquid and gaseous states computed via the Redlich–Kwong equation of state.
(5) The total amount of adsorption A is computed via eqn (21).
(6) The value of pressure is increased to a higher level as required.
(7) The results of predicted adsorption isotherms are output.

Adsorption isotherms for methane on MS-13X at 273·15 K with the pressure ranging 86·43–2498·84 torr, and at 298·15 K with the pressure ranging 149·89–3832·18 torr, are predicted according to the procedures given in Fig. 8. The average of the error between the values of experiment

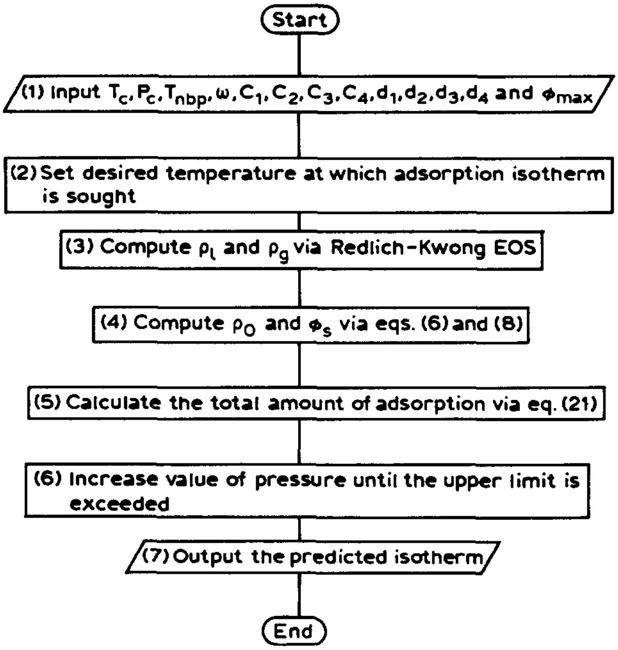

Fig. 8. Computation procedure for prediction of the adsorption isotherm.

and prediction is 9·3% which is sufficiently high for industrial process designs.

With the characteristic parameters evaluated from one set of adsorption equilibrium data for pure nitrogen on MS-13X, isotherms of any temperature of adsorption systems comprising any pure gas adsorbates and MS-13X, at any temperature, can be predicted. Bearing in mind that there is available in the published literature at least one isotherm for known adsorbents, the characteristic parameters of all these known adsorbents could be evaluated using these adsorption isotherms. Consequently, adsorption isotherms of any pure gases on these adsorbents could be predicted using the method described above. Therefore, a database for the adsorption isotherms could be built using this method. The existing adsorption isothermal data could be used as checking points.

3 CONCLUSIONS

The proposed method for predicting the adsorption isotherms using characteristic parameters of adsorbents was proved to be effective and reasonably accurate by industrial standards. The assumptions concerning the characteristics of the adsorbate phase are supported by the results from data processing of the adsorption isotherms. An attractive advantage of this prediction method is that one only needs the characteristics of adsorbents defined and the thermodynamic characteristics of the adsorbate which are readily available in the literature to predict the adsorption isotherms. Since the characteristic parameters of the adsorbents can be evaluated using adsorption isothermal data available in the literature, this method provides a unique and convenient approach for predicting adsorption isotherms and for constructing databases of adsorption equilibrium.

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