VIRIAL-TYPE THERMAL EQUATION OF GAS–SOLID ADSORPTION

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Abstract—A thermal adsorption equation in a virial form is proposed in order to describe the pressure and temperature dependence of adsorption data. This equation permits the elaboration of a method for calculating the isosteric heat of adsorption and for studying its behaviour over a wide range of temperatures and pressures.

INTRODUCTION

Adsorption on solid adsorbents is a fundamental process in the separation of mixtures as well as in the purification of gases. In order to utilize the physical adsorption in the modeling and design of these processes, a quantitative characterization of adsorption equilibria is needed over a wide range of pressures and temperatures. Knowledge of the adsorption models is also needed for correlation and prediction of the equilibrium data in order to minimize the number of experiments. The general equation for the adsorption equilibrium can be written in the following form:

$$F(v, p, T) = 0. \tag{1}$$

The knowledge of the above relationship is of great importance because it allows the estimation of the basic thermodynamic characteristics of an adsorption system and the prediction of adsorption loading as a function of pressure and temperature. The problem of the temperature dependence of adsorption has been studied in many theoretical and experimental works (Barrer and Gibbons, 1963; Pierotti and Thomas, 1971; Cole *et al.*, 1974; Gregg and Sing, 1976; Chan *et al.*, 1984).

The objective of this study was to derive a thermal adsorption equation independent of any adsorption model and use that equation for studying the pressure and temperature dependence of adsorption data.

THEORY

Two basic assumptions are postulated for an adsorption equation:

(1) The adsorption isosteres are linear and described as follows:

$$\left[\frac{\partial \ln p}{\partial (1/T)} \right]_v = g(v) \tag{2a}$$

and

$$\left[\frac{\partial g(v)}{\partial T} \right]_v = 0 \tag{2b}$$

where $g(v)$ is a function dependent only on the amount adsorbed. This assumption was confirmed experi-

mentally [e.g. Seliverstova *et al.* (1978), Fomkin (1986) and Bakayev and Dubinin (1987)].

(2) Its agreement with Henry's law in the low-coverage region:

$$\lim_{v \to 0} v = K_H p. \tag{3}$$

Equation (2a) can be integrated taking into account eq. (2b):

$$\ln p = g(v)/T + f(v) \tag{4}$$

where $f(v)$ like $g(v)$ is a function dependent only on the amount adsorbed. To satisfy condition (3) the function $f(v)$ should tend to a logarithmic function at the limit of $v \to 0$. Analytical forms for both functions are unknown *a priori* and their selection can be realized either by analogy to other adsorption equations or by the best fit of eq. (4) to experimental data. The most convenient way is to use the functions which are linear in relation to the parameters. In this work functions $g(v)$ and $f(v)$ are represented as polynomials of v and then eq. (4) assumes the form

$$\ln p = \frac{1}{T} \sum_{i=0}^{n1} a_i v^i + \sum_{i=0}^{n2} b_i v^i + \ln v \tag{5}$$

where a_i and b_i are adjustable parameters.

The particular case of eq. (5) was derived by Bezus *et al.* (1971) for $n1 = n2$ on the basis of the exponential virial adsorption equation. A similar approach was suggested by Cole *et al.* (1974) and Jaroniec and Jaroniec (1977) for the analysis of the adsorption data on active carbons and zeolites. In these works the fitting of data was carried out for each temperature separately and then the thermal equation parameters were found from the temperature dependence of coefficients.

In the present approach, the number of linear parameters is unknown and $n1 \neq n2$. Equation (5) is considered to be empirical, although the parameters a_o and b_o are directly connected with quantities having a physical meaning, namely

$$q_o = -R a_o \tag{6}$$

Table 1. Test of virial-type thermal adsorption equation for various systems

Adsorbent	Adsorbate	Temperature (K)	Maximum pressure (kPa)	$n1$	$n2$	σ^2	s_v^2	$-\ln K_o$ (mol/g Pa)	$-q_o$ (kJ/mol)	Reference
Active carbon BPL	CH_4	212.7	3830.0	1	3	0.0535	0.0081	25.261 (25.371)	16.43 (16.24)	Reich et al. (1980),
	C_2H_6	260.2	1710.9	4	2	0.0722	0.0093	25.096	21.78	Sircar (1984a, b)
	C_2H_4	301.4	1696.4	1	4	0.1271	0.0090	25.601 (25.459)	23.32 (22.15)	
	CO_2		3841.1	3	2	0.0343	0.0070	26.418 (26.545)	21.62 (21.52)	
Active carbon NuxitAl	CH_4	293	681.1	3	1	0.0390	0.0101	26.344	20.08	Szepesy and
	C_2H_6		670.4	5	1	0.0496	0.0058	27.465	31.20	Illes (1963a, b)
	C_3H_8	313	678.7	5	1	0.0929	0.0081	29.149	42.94	
	$i\text{-}C_4H_{10}$	333	130.2	4	1	0.3048	0.0203	34.520	46.25	
	C_2H_4	363	648.4	3	1	0.0476	0.0080	27.483	29.70	
	C_3H_6		803.5	4	2	0.1448	0.0156	29.455	42.50	
	C_2H_2		118.4	4	1	0.0409	0.0062	34.053	29.42	
	CO_2		743.8	4	1	0.0681	0.0159	27.282	25.68	
Molecular sieving carbon MSC-5A	CH_4	278.6	87.2	5	1	0.0825	0.0184	26.494	20.39	Nakahara et al.
	C_2H_6	303.2	89.6	3	1	0.0424	0.0062	29.734	39.35	(1974)
	C_3H_8	323.2	85.3	5	1	0.1838	0.0178	24.928	35.70	
	$i\text{-}C_4H_{10}$		86.0	4	2	0.2798	0.0196	36.606	54.21	
	C_2H_4		90.8	4	1	0.0560	0.0094	28.302	35.27	
	C_3H_6		90.8	4	1	0.1332	0.0154	29.702	46.96	
Active carbon BPL	CO_2	303 313 323	101.6	3	1	0.0527	0.0130	21.971	12.51	Meredith and Plank (1967)
	N_2	303 313	96.7	3	1	0.0489	0.0168	34.475	42.77	
Carbon black Spheron-6	CH_4	311.0 327.7 344.3 361.0 377.7 394.3	68,564.6	5	3	0.1390	0.0194	29.884	21.57	Don Stacy et al. (1968)

Zeolite NaX	Kr	120, 140 170, 200 220, 270 303.15	12,589.2	6	4	0.0561	0.0091	18.279	15.07	Selivertova et al. (1978)
	Xe	320, 370 400, 450 500, 600	12,589.2	6	4	0.0575	0.0092	18.787	20.60	
Molecular sieve 5A	O_2	273.55	404.8	2	1	0.0234	0.0055	26.269 (26.166)	14.12 (13.91)	Vereist and Baron (1985)
	N_2	298.55	442.9	2	1	0.0202	0.0053	27.993 (27.643)	21.45 (20.42)	
	Ar	319.85 347.95	438.7	2	1	0.0271	0.0040	26.184 (26.151)	13.61 (13.59)	
Molecular sieve 10X	O_2	144.3	212.4	3	1	0.0418	0.0046	25.958 (25.781)	12.85 (12.53)	Nolan et al. (1981) Cohran et al. (1985)
	N_2	172.0 227.6 273.2	212.4	4	2	0.0422	0.0042	27.242 (26.431)	20.86 (17.96)	
	CO	273.2	212.4	4	4	0.1711	0.0070	23.173 (21.478)	15.94 (12.45)	
Molecular sieve 13X	C_2H_6	273.2 298.2 323.2 373.2	137.84	4	1	0.0998	0.0195	27.297 (26.703)	27.75 (25.24)	Hyun and Danner (1982), Cohran et al. (1985)
	$i\text{-}C_4H_{10}$	298.2 323.2 373.2	137.84	4	2	0.0726	0.0105	26.121 (25.058)	32.18 (33.11)	
	C_2H_4	298.2 323.2 373.2	137.84	4	3	0.0817	0.0094	28.638 (27.400)	36.44 (34.40)	
	CO_2	298.2 323.2	137.84	4	3	0.0776	0.0080	35.732 (36.138)	58.29 (59.13)	

and

$$K_H = K_o \exp[q_o/(RT)] \qquad (7)$$

$$K_o = \exp(-b_o). \qquad (8)$$

It may be easily shown that eq. (5) can be utilized directly for estimating an isosteric heat of adsorption as a function of coverage because

$$q_{st}(v) = -R\left[\frac{\partial \ln p}{\partial(1/T)}\right]_v = -Rg(v)$$

$$= -R \sum_{i=0}^{n1} a_i v^i. \qquad (9)$$

RESULTS AND DISCUSSION

The applicability of the virial-type thermal adsorption equation suggested in this work was tested for adsorption data available from the literature. The fitting of the experimental data was carried out by a nonlinear least-square optimization procedure in which the points were weighted according to their estimated errors:

$$\sigma^2 = (1/N) \sum_{j=1}^{N} (\ln p_j^{exp} - \ln p_j^{eq \cdot})^2. \qquad (10)$$

The goodness-of-fit was determined by consideration of the following criteria:

(1) The powers of both polynomials at which error (10) exhibits a minimum and subsequently does not decrease significantly corresponds to the best fit of the experimental points.

(2) A dispersion of errors for all experimental points should be statistically random and independent of temperature.

(3) The error in fitting the value v exhibits a minimum too. This error is here defined as

$$s_v^2 = \sigma_v^2/v_{max} \qquad (11a)$$

$$\sigma_v^2 = (1/N)\left[\sum_{j=1}^{N} \Delta \ln p_j/\Delta v_j\right]^2 \qquad (11b)$$

$$\Delta \ln p_j/\Delta v_j \approx d \ln p_j/dv_j = (1/T) \sum_{i=1}^{n1} a_i v_j^{i-1}$$

$$+ \sum_{i=1}^{n2} b_i v_j^{i-1} + 1/v_j. \qquad (11c)$$

Error (11a) can be considered as the measure of dispersion along the v-axis.

(4) A further criterion involved the visual inspection of the fit between the experimental points of various polynomials.

Table 1 summarizes the results of applying this fitting procedure to data analysed in this work. Table 1 includes the values of errors in $\ln p \, (\sigma^2)$ and $v \, (s_v^2)$, isosteric heats at zero coverage and K_o (the limiting value of Henry's constant at $T \to \infty$). The values in parentheses are given to compare the present results and results available from the literature. As can be seen the results are strikingly similar.

Figure 1 shows the best-fit solid-line curves for adsorption of methane on BPL active carbon at three different temperatures (Reich et al., 1980). Figure 2 depicts the dispersion of errors σ_j^2 for experimental points. It may be seen that eq. (5) describes the isotherm data extremely well and the error does not exceed the limit of 5%.

The course of the isosteric heat of adsorption in the dependence of the amount adsorbed for the above system is shown in the Fig. 3. The heat of adsorption is
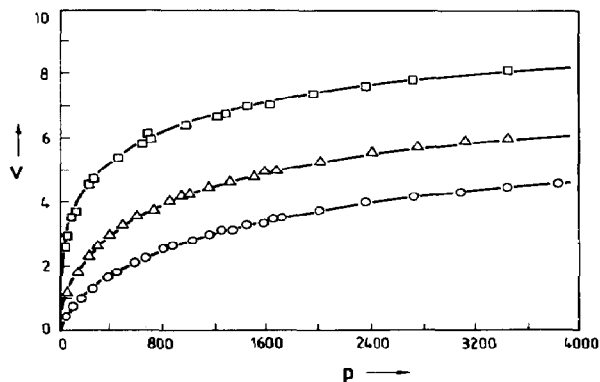

Fig. 1. Comparison of predicted and experimental data for methane on active carbon BPL at 212.7 K ($\square$), 260.2 K ($\triangle$), and 301.4 K ($\bigcirc$) (Reich et al., 1980) (v in mg-mol/g C, p in Pa).
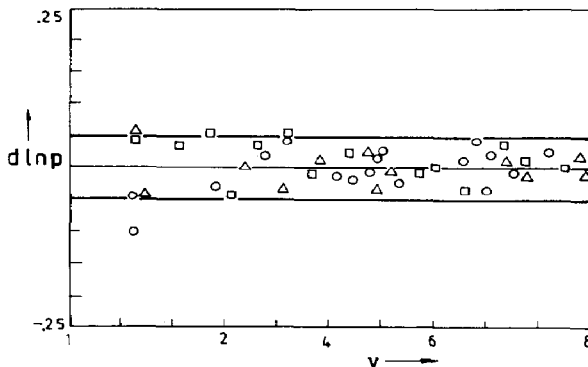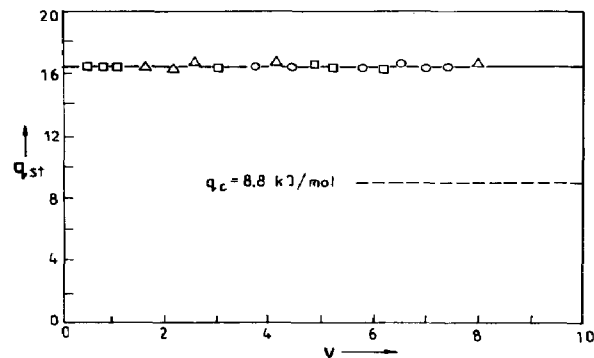

Fig. 2. Error in fitting experimental data.

Fig. 3. Isosteric heats of CH_4 adsorption on active carbon BPL ($q_c = CH_4$ heat of condensation) (q_{st} in kJ/mol, v in mg-mol/g C).

practically constant and only a small decline indicates the heterogeneity of the surface. The isosteric heat of adsorption is higher than the heat of condensation and is enough to be characterized as physical adsorption. In order to demonstrate the temperature invariance of the heat of adsorption the experimental points considered were plotted in Fig. 3 according to

$$q_{st}(v_{exp}) = R(-\ln p_{exp}) + g(v_{exp}) + \ln v_{exp}. \quad (12)$$

CONCLUSIONS

It may be concluded from the above observations that adsorption data are well analysed by using a virial-type thermal adsorption equation since it gives a good representation of the data. It allows one to describe and predict the isothermal data over a large range of temperatures, below and above the critical temperature of the adsorbate, and for pressures from subatmospheric to a high-pressure region. Equation (5) can be useful in elaborating a method for calculating the isosteric heats of adsorption and other physicochemical characteristics for different adsorption systems. This method compared with the well-known graphical method based on the Clausius–Clapeyron equation shows an advantage because it permits the minimization of deviations for all experimental points measured over a wide range of pressures and temperatures. The adsorption data for analysis need not be determined as a pencil of isotherms but could be obtained for instance by a so-called isosteric method (Kadlec and Dubsky, 1975) or as a set of points from a definite range of temperatures and pressures (Czepirski, 1987).

NOTATION

a	adjustable parameter in eq. (5)
b	adjustable parameter in eq. (5)
K_H	Henry's constant, mol/g Pa
K_0	limiting value of K_H at $T \to \infty$, mol/g Pa
$n1, n2$	number of parameters in thermally dependent and thermally independent term of eq. (5), respectively
N	number of experimental points
p	equilibrium pressure, Pa
R	gas constant, J/mol K
q_{st}	isosteric heat of adsorption, kJ/mol
q_o	adsorption heat at zero coverage, kJ/mol
T	absolute temperature, K
v	amount adsorbed, mol/g
v_{max}	maximum amount adsorbed for a given adsorption system, mol/g
s_v^2, σ_v^2	errors of fitting value of v
σ^2	error of fitting value of $\ln p$

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