JOURNAL OF MATERIALS SCIENCE **37** (2002) 885–893

Characterisation of structural parameters of finely divided and porous materials by a new adsorption isotherm

P. T. JOHN
C-1/1027, Vasant Kunj, New Delhi, 110 070, India

V. S. ACHARI
School of Environmental Studies, Cochin University of Science and Technology, Lakeside Campus, Fine Arts Avenue, Cochin - 682016, India
E-mail: vsachari@cusat.ac.in

An adsorption isotherm $\log\log p = C + n \log v$ was developed and applied earlier. The isotherm has been used to determine the structural parameters of adsorbents. The application of the isotherm has been extended to determine separation factor of mixture of gases, surface area of adsorbed monolayer from energy consideration, categorisation of micropores etc. It is shown that equation of Lewis *et al.* for partial adsorption and equation of Langmuir can be deduced from isotherm equation of John. Advantages of John's isotherm are enumerated. © *2002 Kluwer Academic Publishers*

1. Introduction

Adsorption studies are very useful to determine the structural parameters of finely divided and porous materials. Basic understanding of mixture adsorption is essential for practical applications in chemical industries, separation and purification of gases, recovery of industrial solvents etc. There are many adsorption isotherm equations which can be applied to determine the parameters of adsorbents. A review of the application of John's isotherm has been published earlier [1–4]. Since then the applicability has been extended to determine many other parameters. This is a review of the latest applications of the isotherm [5–19].

2. Dubinin-Astakhov and John's isotherms

Almost all the working isotherms, specially in the micropore region are analytical in nature. Such an isotherm given by Dubinin and Astakhov [5–9] is

$$\log v = \log v^{o} - D \log(p^{o}/p)^{m} \qquad (1)$$

meaning of symbols are given in appendix. It is not possible to plot Equation 1 without knowing the value of 'm'. The 'm' is chosen by trial till Dubinin plot $\log v$ versus $(\log p^{o}/p)^{m}$ gave a straight line. In Fig. 1 plot B and E are according to Equation 1. Plot E is a straight line when the corresponding value of 'm' is 1.5. But plot B is not a straight line when the value of 'm' > 1.5 John's isotherm is given by

$$\log\log p = C + n \log v \qquad (2)$$

In Fig. 1 plot A is John's isotherm. It can be plotted directly from data. This is an important advantage of John's isotherm. Dubinin's isotherm equation for microporous materials is given by

$$\log v = \log v^{o} - D(\log p^{o}/p)^{2} \qquad (3)$$

Table I [10] shows that the two Equations 2 and 3 give almost identical results.

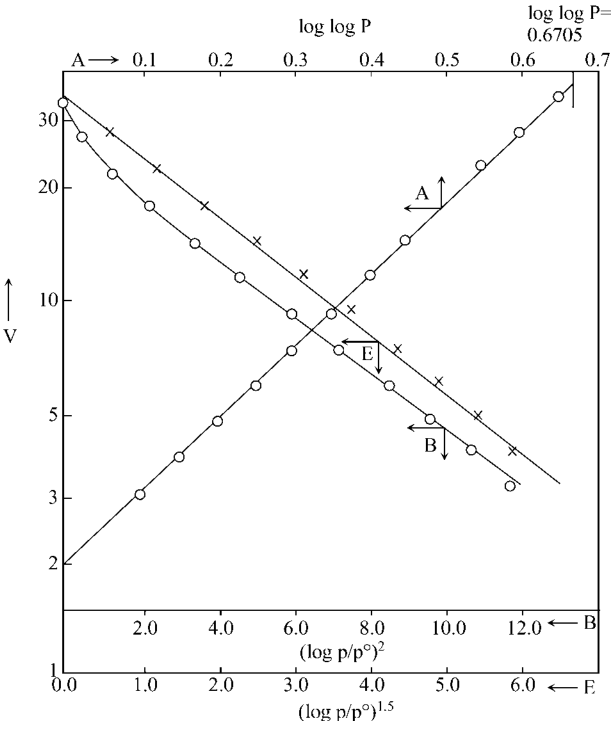

Figure 1 D–A Plots and John's plot for the Adsorption of CO_2 at 298 K on Active Carbon. A - John's Plot, B - D–A Plot with $m = 2$, E - D–A Plot with $m = 1.5$.

0022–2461 © *2002 Kluwer Academic Publishers*

TABLE I Comparison of micropore volume obtained by means of Equations 2 and 3

Sl. No.	Adsorbent	Adsorbate	Temperature (°C)	Micropore volume by eqn (2), (m moles/g)	eqn (3) (m moles/g)
1	Ac. carbon 1	C_6H_6	20	0.86	0.82
2	Ac. carbon 2	C_6H_6	20	1.07	1.07
3	Ac. carbon 3	C_6H_6	20	2.43	2.36
4	Ac. carbon 5	C_6H_6	20	5.75	5.91
5	Coconut charcoal	N_2	−196	15.17	15.33

TABLE II Percentage of error introduced in the value of $(\log p^o/p)^2$ and $\log\log p$ when 5% error is in the value of $p/p^o = 100$ cm

Pressure in cm				% error in the case of	
Correct	With −5% error	$(\log p^o/p)^2$ (Dubinin)	$\log\log p$ (John)	$(\log p^o/p)^2$	$\log\log p$
20		0.4886	0.1142		
	19.0	0.5214	0.1069	6.7*	−6.4**
30		0.2730	0.1694		
	28.5	0.2973	0.1629	8.9	−3.8
50		0.0906	0.2303		
	47.5	0.1045	0.2245	15.5	−2.5
80		0.0094	0.2795		
	76.0	0.0142	0.2747	51.1	−1.8
	With +5% error				
20		0.4886	0.1142		
	21.0	0.4594	0.1212	−6.0	6.2
30		0.2730	0.1694		
	31.5	0.2517	0.1756	−7.8	3.7
50		0.0906	0.2303		
	52.5	0.0783	0.2231	−13.6	2.3
		0.0094	0.2795		
80	84.0	0.0057	0.2842	−39.4	1.7

*6.7 (column 5) = [(0.5214–0.4886)/0.4886] 100

**−6.4 (column 6) = [(0.1069–0.1142)/0.1142] 100

3. Effect of errors in the value of *p* on $\log\log p$ and $(\log p^o/p)^2$

Effect of errors in the value of p on the values of $\log\log p$ and $(\log p^o/p)^2$ can be calculated by imposing a known percent of error (say 5%) in the value of p and then calculating $\log\log p$ and $(\log p^o/p)^2$. Table II shows the results. It is evident from Table II that error in the values of $\log\log p$ is of the same order and sign as that of imposed error in p. On the other hand the error in the value of $(\log p^o/p)^2$ increases with pressure and the sign of error is opposite to that of imposed error. The above facts show that John's method of calculation will give less error. It may be noted that the term $\log\log p$ comes in John's isotherm equation and the term $(\log p^o/p)^2$ comes in Dubinin's isotherm equation.

4. Separation factor from John's isotherm

The process of separation and purification of gases is of vital importance in many problems in chemical engineering. The process is widely used in adsorbent column, petrochemical industries, petroleum refining etc. With an equivalent number of theoretical stages as in distillation unit, much higher separation factor are commonly attainable in an adsorption system. In order to apply adsorption separation process one has to find a suitable adsorbent with a suitable separation factor. Separation factor S of a binary mixture is defined as [11, 12]

$$S = (x_1/y_1)/(x_2/y_2) \tag{4}$$

where x_1 and x_2 are adsorbed mole fractions of gas 1 and gas 2 and y_1 and y_2 are mole fractions gas 1 and gas 2. John's adsorption isotherms for components and binary mixture of gases are given by [11, 12]

$$\log\log p_1^o = C_1 + n_1 \log v_1^o \tag{5}$$

$$\log\log p_2^o = C_2 + n_2 \log v_2^o \tag{6}$$

and

$$\log\log p_{12} = C_{12} + n_{12} \log v_{12} \tag{7}$$

It was shown earlier [1, 11, 12] that

$$n_{12} = n_1 y_1 + n_2 y_2 \tag{8}$$

and

$$C_{12} = C_1 y_1 + C_2 y_2 \tag{9}$$

Note that $y_1 + y_2 = 1$. It was stated earlier that [1] n is a function of adsorbability. Hence it is reasonable to assume that the ratio of partial adsorption to total adsorption (*i.e.*, v_1/v_{12}) at any total pressure p_{12} is equal to the ratio of n value contributed by component 1 to total n value contributed by mixture (*i.e.* $n_1 y_1/n_{12}$). Thus, adsorbed mole fraction x_1 of gas 1 is given by

$$x_1 = n_1 y_1/n_{12} \tag{10}$$

and

$$x_2 = n_2 y_2/n_{12} \tag{11}$$

the mole fraction of component i adsorbed is $x_i = niyi/n_{12} = vi/v_{12}$. The component i adsorbed is given by $vi = xiv_{12}$. Dividing Equation 10 by 11 one gets

$$(x_1/y_1)/(x_2/y_2) = n_1/n_2 \tag{12}$$

Table III shows the values of S and n_1/n_2. It is clear that separation factor S and the ratio of adsorbability n_1/n_2 are the same or $S = n_1/n_2$.

5. Conversion of John's partial adsorption equation to Lewis *et al*. [13] partial adsorption equation

Under condition $p_1^o = p_2^o = p_{12}$ multiply John's Equation 5 by y_1 and Equation 6 by y_2 and add them. Equating the r.h.s. of the resultant with the r.h.s. of Equation 7. Now since $y_1 + y_2 = 1$ and in view of Equations 8 and 9, one gets

$$n_1 y_1 \log v_1^o + n_2 y_2 \log v_2^o = n_1 y_1 \log v_{12} + n_2 y_2 \log v_{12} \tag{13}$$

or

$$n_1 y_1 \log \left(v_{12}/v_1^o\right) = -n_2 y_2 \log v_{12}/v_2^o \tag{14}$$

TABLE III Comparison of S and n_1/n_2 values of binary mixture adsorption

Adsorbent	Activated carbon 33		Cs1		Molecular sieve
Temperature (K)	293	343	77.49	83.56	298
Adsorbate					
Component 1 (%)	CH_3OH (70)	CH_3OH (50)	O_2(75)	N_2(60)	C_2H_6(60.7)
Component 2 (%)	C_2H_5OH (30)	C_2H_5OH (50)	Ar (25)	CO (40)	C_2H_4 (39.3)
S	0.419	0.545	1.1	5.87	0.483
n_1/n_2	0.455	0.565	1.06	5.87	0.483

Dividing the above equation by n_{12} one gets

$$(n_1 y_1/n_{12}) \log v_{12}/v_1^{\mathrm{o}} = -(n_2 y_2/n_{12}) \log v_{12}/v_2^{\mathrm{o}} \tag{15}$$

John's partial adsorption equations from binary mixtures are

$$n_1 y_1/n_{12} = v_1/v_{12} \quad \text{and} \quad n_2 y_2/n_{12} = v_2/v_{12}$$

Substituting this relation in Equation 15 one gets

$$v_1/v_{12} \log\left(v_{12}/v_1^{\mathrm{o}}\right) = -v_2/v_{12} \log\left(v_{12}/v_2^{\mathrm{o}}\right) \tag{16}$$

Substituting the approximations

$$-\log v_{12}/v_1^{\mathrm{o}} \cong \left(1 - v_{12}/v_1^{\mathrm{o}}\right)a$$

and

$$-\log v_{12}/v_2^{\mathrm{o}} \cong \left(1 - v_{12}/v_2^{\mathrm{o}}\right)a$$

in Equation 16 one gets

$$v_1/v_1^{\mathrm{o}} + v_2/v_2^{\mathrm{o}} = 1 \tag{17}$$

This is Lewis *et al.* equation for partial adsorption. Fig. 2 shows the plot between $(-\log x)/a$ and x and $(1 - x)$ versus x. Note that the two plots coincide.

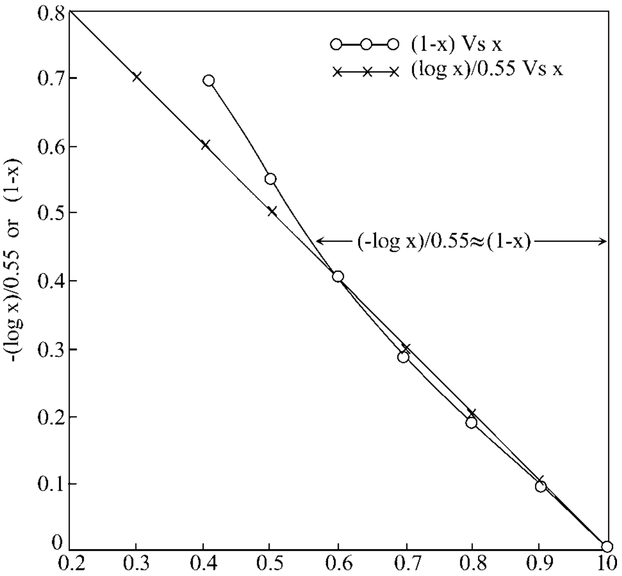

Figure 2 Graph between x and $(1 - x)$ or between x and $-(\log x)/0.55$.

6. Surface area of adsorbents from surface energy

It was mentioned [2] that when adsorption data of non-microporous adsorbents are plotted according isotherm of John, they give straight lines with kinks or sudden changes in slope or discontinuity. The amount adsorbed corresponding to the first kink invariably gave monolayer capacity. Once the monolayer capacity is known S_w the surface area can be determined by the application of Equation of Reich [14] modified by John and Aggarwal [15]. The equation is given by

$$S_w = [(2.303 V_m \mathrm{RT}(\log V_v/V_f))/4\gamma]V \tag{18}$$

where V_v and V_f are respectively molar volumes of gas and liquid at temperature of adsorption and γ is surface energy per unit area of adsorbent at adsorption temperature and V is the molar volume of gas at S.T.P. The advantage of this equation is that one can find area without reference to molecular area of adsorbate molecule. The results are given in Table IV. When binary mixture is adsorbed the specific area is given by

$$S_w = [(2.303\ \mathrm{RT}\log(V_{v12}/V_{f12}))/4\gamma_{12}](V_{m12}/V) \tag{19}$$

where v_{m12} is the volume of mixture adsorbed at S.T.P., V is molar volume at S.T.P. for all gases and mixtures, V_{v12}, V_{f12} and γ_{12} are respectively molar volumes of vapour mixture, liquid mixture adsorbates and surface energy of liquid mixtures at adsorption temperature T. These are given by [20]

$$V_{v12} = v_{v1} y_1 + v_{v2} y_2 \tag{20}$$

$$V_{f12} = v_{f1} y_1 + v_{f2} Y_2 \tag{21}$$

$$\gamma_{12} = \gamma_1 y_1 + \gamma_2 y_2 \tag{22}$$

Here y_1 and y_2 are mole fractions of gas 1 and gas 2 respectively. Saturation vapor pressure of mixture was assumed to be sum of saturation vapour pressure of each gas multiplied by its mole fraction. V_m or V_{m12} was found by BET method or any other method. Partial adsorption V_1 and V_2 were found by equation developed by John [18]. They are

$$V_1 = (n_1 y_1/n_{12})V_{12} \tag{23}$$

and

$$V_2 = (n_2 y_2/n_{12})V_{12} \tag{24}$$

TABLE IV Monolayer capacity and surface area by surface energy method^x

		Monolayer capacity (cc/g)				Surface area (m^2/g)			
Adsorbate	Adsorbent	Langmuir (Published)	John (Calculated)	v_{m1}	v_{m2}	S_w	S_1	S_2	(S_1+S_2)
N_2	Activated Carbon	32.4	30.9	—	—	165.1*	—	—	—
O_2	Activated Carbon	45.2	43.4	—	—	159.6*	—	—	—
Ar	Activated Carbon	41.4	40.5	—	—	153.2*	—	—	—
Mixture (60% N_2 & 40% O_2)	Activated Carbon	—	35.6	22.8	12.8	155.4$^+$	115.9	45.2	161.2
Mixture (60% N_2 & 40% Ar)	Activated Carbon	—	33.8	23.4	10.4	150.2$^+$	119.2	38.5	157.7
Mixture (60% O_2 & 40% Ar)	Activated Carbon	—	42.6	27.9	14.7	153.2$^+$	98.4	54.3	152.8

^{x}Experimentally measured at −183°

*These values have been calculated using equation (2) for a single gas.

$^+$These values have been calculated using equation (3) for binary mixture.

Note: In col. 7, S_w has been calculated either by using equation (2) or (3), while in col. 10, $S_1 + S_2 (= S_w)$ has been calculated by the summation of col. (8) & (9) *i.e.* equation (4), hence the minor difference in the results.

It may be noted that

$$n_{12} = n_1 y_1 + n_2 y_2 \tag{8}$$

n_1 and n_2 are slopes of isotherm using gas 1 and gas 2 respectively. The values of S_1 and S_2 are

$$\begin{aligned} S_w &= S_1 + S_2 \\ &= [(2.303\ \mathrm{RT} \log(V_{v1}/V_{f1}))/4\gamma_1](V_{m1}/V) \\ &\quad + [(2.303\ \mathrm{RT} \log(V_{v2}/V_{f2}))/4\gamma_2](V_{m2}/V) \end{aligned} \tag{25}$$

The results are given in Table IV. The results support the theories behind the experimental work.

7. Categorisation of micropores from slope and shape of isotherms

John's isotherm is given by

$$\log\log p = C + n \log v \tag{2}$$

when micropore adsorption data are plotted normally they give only one line representing one phase of adsorption. Since in micropore filling there is only one phase of adsorption there will be only one line to represent the adsorptions. The slope of the isotherm is given by [20]

$$n = (\log\log p^{\mathrm{o}} - \log\log p_{\mathrm{o}})/(\log v^{\mathrm{o}} - \log v_{\mathrm{o}}) \tag{26}$$

where p^{o} is saturation pressure when the amount adsorbed is v^{o} and p_{o} is a low pressure when the amount absorbed is v_{o}. The magnitude of n will depend on the difference between v^{o} and v_{o}. Mainly there can be three cases: (a) when $v^{\mathrm{o}} \gg v_{\mathrm{o}}$, (b) when $v^{\mathrm{o}} > v_{\mathrm{o}}$ and (c) when $v^{\mathrm{o}} \cong v_{\mathrm{o}}$. The effect of the three conditions are shown by means of Table V. Micropores can also be categorised from slope of isotherms as shown by means of Table VI. Figs 3–6 show the typical distribution of

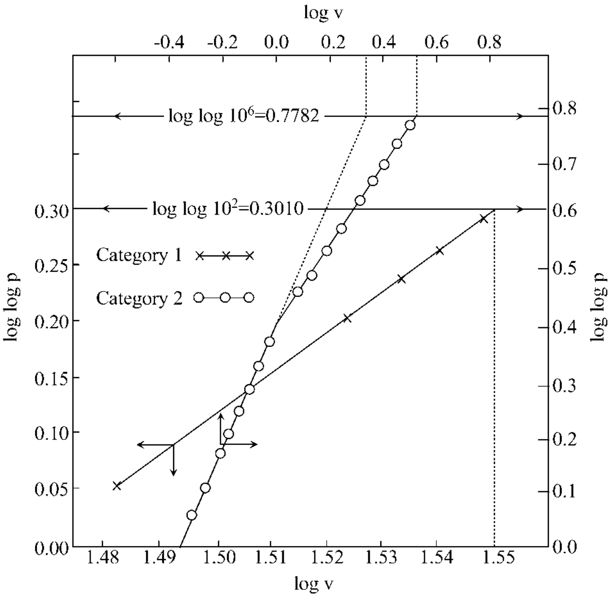

Figure 3 Adsorption of N_2 on charcoal [6] (0.2 g) at −195.5°C (Cat. 1) and adsorption of C_6H_6 on active carbon [20] D_2 at 20°C (Cat. 2).

TABLE V Categorisation of microporous carbons from the slope of isotherms

	Comparative values of					Degree of microporosity		
Sl. No.	v_l or $\log v_l$	v_s or $\log v_s$	Relation of v_l to v_s	Slope 'n'	Range of micropores	finer	coarser	Remarks & example
1	large	large	nearly equal	large	narrow	large	negligible	Curve B_3 of Figure 5
2	small	small	nearly equal	large	narrow	small	negligible	Curve B_1 of Figure 5
3	small	large	$v_s > v_l$	small	wide	small	large	Curve B_5 of Figure 5

In case of Sl. Nos. 1 & 2 when the range of micropores is very narrow, highly uniform pores are obtained.

TABLE VI Categorisation of microporous carbon from the shape of isotherm

Cat.	Description of isotherms	Dispersion of pores and indications	Remarks
1	One line connects all the exptl. points. Figure 3	Monodisperse pores. Eg. Carbon from sucrose & veg. stock	v_s and LMV* is obtained by extrapolation
2	Two lines connect all the exptl. points. Figure 3	Bidispherse pores Eg. carbon from coals	Extrapolation of upper and lower lines respectively gives v_t (total LMV) & v_f (LMV of finer pores). v_c the LMV of coarser pores is equals $v_t - v_f$
3	One line joins all the lower exptl. points. Upper points deviate more and more away from the extrapolated line joining the lower points. Figure 4	Monodisperse micropores plus mesopores. Adsorption on mesopores causes the deviation of upper points from extrapolated line	Extrapolation of line joining the lower points gives v_s the LMV. Adsorption capacity is V_s. Hence $v_{me} = V_s - v_s$
4	Nearly parallel isotherm of progressively activated carbons. Eq. B_1 & B_2 of Figure 5	Monodisperse. No. change in dispersion of pores with activation	LMV of B_2 is more than that of B_1
	Nonparallel isotherms of progressively activated carbons. Eq. B_3 and B_5 of Figure 5	Monodisperse. Change in dispersion of pores with activation	LMV of B_5 is more than that of B_3
5	Isotherms of progressively activated carbons cross each other Figure 5 B_3 & B_5	Monodisperse. The difference in activation between the two isotherms is not much. Less activated has finer pores compared to more activated. Narrow pores have more intense adsorptive force	Finer pores of less activated will adsorb more at low pressure compared to more activated having coarser pores. The coarser pores of more activated will adsorb more at higher pressure compared to less activated. Hence lower part of less activated will lie on the r.h.s. and its upper part will lie on the l.h.s. of the isotherm of more activated
6	One line joins the lower exptl. points upto cutoff. At cutoff a horizontal line connects exptl. points. Figure 6	Monodisperse upto cutoff. Pores above a certain size is not existing	Extrapolation will not give correct LMV
7	Isotherm has an upward deviation at very low pressure range. Figure 6	Some pores of adsorbent are smaller than adsorbate molecules	Activated diffusion and molecular sieve effects at low pressures
8	The isotherm is represented by a steep line C of Figure 5	Monodisperse. Indicates the rane of micropores is very narrow and a high n value	The amount adsorbed at any pressure is not much different from that at $p/p_s = 1$
9	One line connects all the exptl points of adsorption. Another line shows the desorption	Monodisperse	Trapping of adsorbate or adsorption induced strains cause hysteresis

*Limiting Micropore Volume.

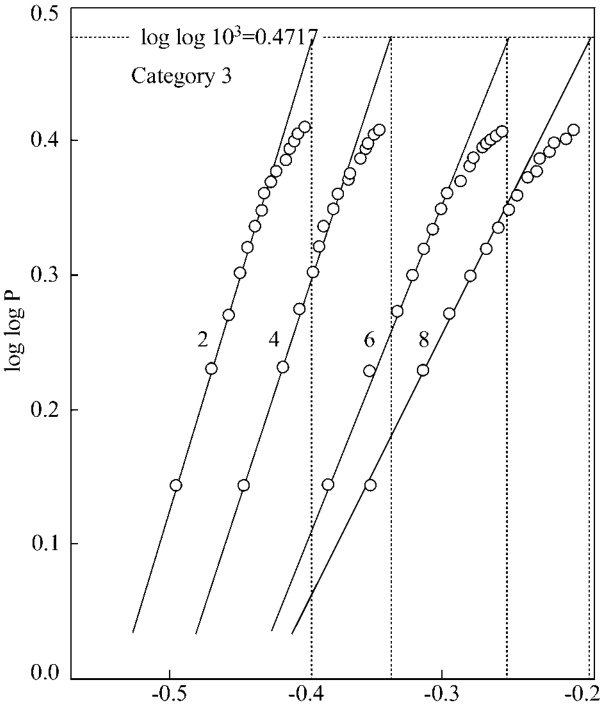

Figure 4 Adsorption of benzene on progressively activated charcoal [20] (AU_2–AU_8).

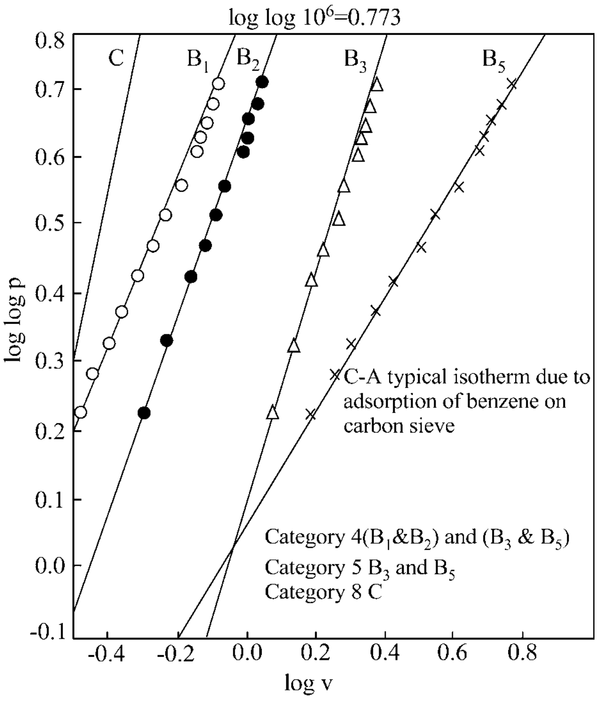

Figure 5 Adsorption of benzene on progressively activated carbons [20] B_1, B_2, B_3 and B_5 at 20°C.

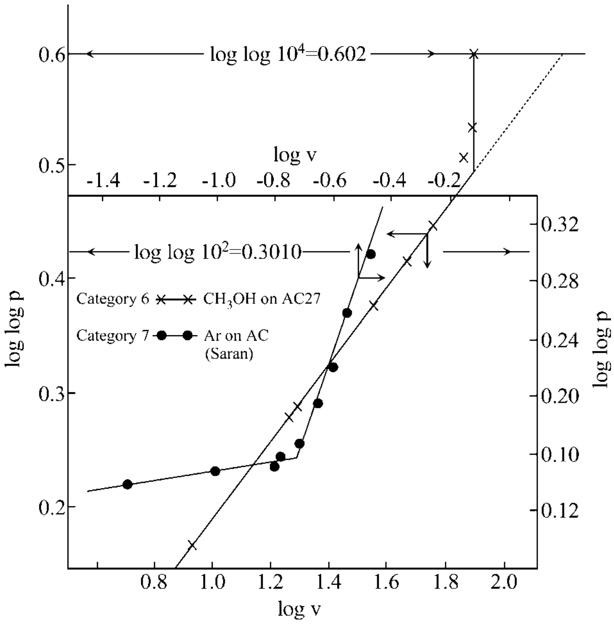

Figure 6 Adsorption of methanol on activated carbon (AC27) at 20°C and adsorption of argon on saran carbon [20] at $-196.2°$C (Cat. 6 and 7).

micropore volume (category 1, 2, and 6 and 7) of microporous carbons.

8. Transformation of John's isotherm equation to Langmuir equation

Adsorption potential E is given by [16]

$$E = 2.303\ \mathrm{RT} \log p_s/p \tag{26}$$

John expressed adsorption potential in terms of amount adsorbed as [2]

$$E = 2.303\ \mathrm{RT}B_o \log v_s/v \tag{27}$$

Equating Equations 26 and 27 one gets

$$\log p_s/p_o = B_o \log v_s/v \tag{28}$$

Substituting the approximations

$$\log p_s/p \fallingdotseq -(1 - p_s/p)/A \tag{29}$$

and

$$\log v_s/v \fallingdotseq -(1 - v_s/v)/a \tag{30}$$

in Equation 28 one gets

$$(1 - p_s/p)/A = (1 - v_s/v)B_o/a \tag{31}$$

Hence

$$(a/B_oA)(1 - p_s/p) = (1 - v_s/v)$$

or

$$p/v = p/v_s(1 - a/B_oA) + ap_s/B_oAv_s \tag{32}$$

Neglect the second terms of $(1 - a/B_oA)$ since it is much smaller than 1 and put $ap_s/B_oA = 1/b$. Hence Equation 32 becomes [6]

$$p/v = p/v_s + 1/v_sb \tag{33}$$

This is the Langmuir equation.

9. Effect of temperature below and above critical temperature on mixture of gases

John's adsorption equation is given by

$$\log\log p = C + n \log v \tag{2}$$

If a binary mixture of gas is used the adsorption isotherms for gas 1, gas 2 and the mixture are

$$\log\log p_1 = C_1 + n_1 \log v_1 \tag{5}$$

$$\log\log p_2 = C_2 + n_2 \log v_2 \tag{6}$$

and

$$\log\log p_{12} = C_{12} + n_{12} \log v_{12} \tag{7}$$

where

$$n_{12} = n_1y_1 + n_2y_2 \tag{8}$$

and

$$C_{12} = C_1y_1 + C_2y_2 \tag{9}$$

Total adsorption v_{12} from binary mixture is given by Equation 7

All the values of symbols except v_{12} are known. Hence v_{12} can be calculated. C_1, C_2, n_1 and n_2 are obtained from the plots of above equations. John [18] showed that the ratio of partial adsorption v_1 to total adsorption v_{12} (*i.e.* v_1/v_{12}) at any pressure is equal to the ratio of $n_1y_1/n_{12}y_{12}$, the n value contribution of first component to the n value contribution n_{12} of the mixture. Mole fraction x_1 of first component is given by

$$x_1 = y_1n_1/n_{12} = v_1/v_{12} \tag{10}$$

Similarly

$$x_2 = y_2n_2/n_{12} = v_2/v_{12} \tag{11}$$

The component adsorbed is given by

$$v_1 = x_1v_{12} \quad \text{and} \quad v_2 = x_2v_{12} \tag{34}$$

Note $x_1 + x_2 = 1$. Validity of Equations were tested by means of published data. Total and partial adsorptions at below and above critical temperature were calculated by applying Equations 7, 10 and 11. Table VII shows the total and partial adsorptions of mixture of nitrous oxide and carbon dioxide at 273 K on active carbon. It is seen that the calculated values of total and partial adsorptions agree well with the published experimental values when the temperature is below critical temperature. Adsorption of N_2-O_2 binary mixture on

TABLE VII Experimental data to show the validity of Equations 7 and 11 to determine total and partial adsorptions. Adsorption of N_2O and CO_2 mixture on carbon at 0°C (below critical temperature). Gas phase composition: CO_2 23.4%, N_2O 76.6%

Total pressure (mm. Hg)	Total amount adsorbed in cc		Partial adsorption of CO_2 in cc	
	Published	Calculated	Published	Calculated
77.3	28.9	27.1	3.9	5.5
137.4	38.9	37.8	5.8	7.7
220.1	48.9	48.2	8.1	9.8
322.6	58.8	57.8	10.4	11.8
431.0	66.2	65.7	13.2	13.4
607.4	75.3	76.2	14.7	15.5
1011.6	92.3	93.3	19.7	19.0
1287.3	99.5	101.9	21.9	20.8
1610.4	106.0	111.2	23.7	22.7

$n(CO_2 = 0.3273$, $n(N_2O) = 0.3908$
$C(CO_2) = -0.1546$, $C(N_2O) = -0.2957$
$n_{12} = 0.3438$, $C_{12} = -0.1914$

TABLE VIII Adsorption of N_2–O_2 binary mixture on Zeolite −10× at 144.3 K (above critical temperature)

	X_1		V_{12}	
Y_1	Calculated	Published	Calculated	Published
8.8	3.40	4.0	97.0	104.2
22.9	9.44	10.2	105.2	105.7
44.4	21.9	21.7	105.2	107.4
57.2	31.93	28.3	105.7	106.8
76.4	53.2	43.0	106.9	106.9
85.0	64.3	52.2	106.2	107.3
93.8	84.2	67.2	106.2	108.9

Y Vapour phase mole percent, V_{12} total volume adsorbed (cc/g),
X Adsorbed phase mole percent. Subscript '1' means O_2 and '2' means N_2.

zeolite at above critical temperature showed that total adsorption agreed with the experimental values but partial adsorption obtained by calculation was lower than the published values. The above results are shown in Table VIII. Ternary mixture adsorption (total) agreed with experimental values at above critical temperatures Table IX.

10. Monolayer capacity of solids by solute adsorption

Normally data collected for adsorption are pressure or concentration and amount adsorbed. In order to find monolayer capacity isotherm may be drawn between $\log\log p$ (or $\log\log c$) and $\log a$ and the value of 'a' corresponding to the kink or discontinuity is taken as monolayer value. It may be stated that symbol 'a' is for the amount adsorbed and c is concentration of adsorbate.

TABLE X Specific adsorption of aniline on charcoal [24]

Adsorption System	C m. mole/l	a^* m. mole/l	$\log\log C$	$\log a$
Aniline on charcoal from water	4.50	2.579	−0.1850	0.4114
	13.02	3.073	0.0470	0.4874
	19.29	3.296	0.1093	0.5180
	42.12	3.612	0.1812	0.5577
	57.55	3.778	0.2106	0.5772
	75.87	3.949	0.2742	0.5964
	109.80	4.055	0.3098	0.6080
	253.30	4.664	0.3809	0.669
Aniline on charcoal from benzene	15.11	7.501	1.1793	0.8752
	32.79	10.49	1.5157	1.0209
	69.12	14.36	1.8396	1.1571
	112.85	15.72	2.0527	1.1965
	113.36	17.02	2.0555	1.2309
	218.62	20.76	2.3397	1.3173
	282.27	28.93	2.4507	1.4614
	321.10	35.56	2.5106	1.5510

*Specific adsorption a is 10^2 times for benzene medium.

Kunju [24] did a number of adsorption experiments with fortyone systems of solutes applying different isotherm equations. Then he tried to find out the equations applicable to the systems. According to him Harkins–Jura equation is valid for the entire range of concentration studied. We collected published data (Table X) consisting of concentration and the amount adsorbed at constant temperature. Then plotted John isotherm equation

$$\log\log c = C_o + n_o \log a$$

The isotherm consisted of straight line and kink or discontinuity. The $\log a$ corresponding to the first kink was found to be the monolayer value. It is clear that phase change occurs at $\log a = 0.606$ for the adsorption of aniline from water. Hence $a = 4.036$ mmole/g. Published value (Langmuir) is 4.172 mmole/g. For the adsorption aniline from bezene the kink appears at log 1.32, corresponding to $a = 20.89$ mmole/g. Specific adsorption a for adsorption of aniline is in the order of 10^2. Hence the actual value is 0.2089 mmole/g. Langmuir value is 0.2015.

According to Voyutsky [25] adsorption at solid-solution interface is in general similar to that at solid

TABLE IX Adsorption of ternary mixtures of O_2, N_2 and CO on Zeolite −10 × at 144.3 K (above critical temperature)

O_2 conc.		N_2 conc.		CO conc.		Total V_{123} (c.c./g)	
Adsorbed phase (mole%)	Vapour phase (mole%)	Adsorbed phase (mole%)	Vapour phase (mole%)	Adsorbed phase (mole%)	Vapour phase (mole%)	Calculated	Published
16.0	47.3	18.0	36.3	66.0	16.5	112.2	117.6
12.0	40.1	12.3	37.7	75.7	22.2	113.8	118.9
10.0	35.7	9.9	35.0	80.1	29.2	113.8	119.8
8.4	32.0	8.1	32.1	83.6	35.9	117.2	120.7
6.8	27.5	6.2	28.4	87.0	44.2	120.1	121.7

gas interface. In the former case the phenomenon is complicated by the presence of third component (*i.e.* solvent whose molecules may also be adsorbed on the adsorbent surface). Kireev [26] stated that isotherm of dissolved substances have the same general form as those of gases and the same equation holds for them if we substitute the concentration c for pressure p.

It was observed that when John's isotherm is plotted the plot will give different lines representing different phases. When phase change occurs, the plot will give a kink or sudden change in slope or discontinuity in the isotherm. The transition takes place due to changes in adsorbent-adsorbate interaction as more and more adsorption takes place. It is reasonable to identify the first kink or discontinuity as the point where monolayer is completed.

Similarly published data [27] for the specified adsorption of phenol on wood [28] a natural porous material was ploted using D-R, Langmuir and John isotherm relationships. The D-A plots were made on changing value of m as 2.0, 1.5, 1.2, 0.80 and 0.6, such that a line is obtained. For a value of m equal to 0.6 the isotherm becomes a straight line with a monolayer value of 19.185 mg/g at 283 K. The regression coefficient r for the selected value of m were varied from 0.87, 0.91, 0.94, 0.97 and 0.99. The monolayer capacity obtained by Langmuir method is 20.92, 18.38 and 16.26 mg/g at 283, 293 and 303 K respectively. On applying John isotherm, the monolayer obtained are 21.37, 18.62 and 16.218 mg/g, exactly the same value observed for Langmuir model. This confirms the application of John's isotherm for the study of adsorption from solution phase.

11. Advantages of John's isotherm

1. One and the same equation is valid for all types of adsorption.
2. Isotherms can be plotted directly from the data.
3. Different phases of adsorption can be identified from the isotherm.
4. Kink or sudden change in slope of isotherm can be located easily.
5. Only comparatively low pressure adsorption is sufficient to evaluate monolayer capacity from type 1 isotherm or limiting micropore volume.
6. Many well known isotherms like Langmuir, Freundlich, Dubinin etc. can be derived from John's equation with minor approximation.
7. The effect of error in the value of p on $(\log\log p)$ is much lower than on $(\log p_s/p)^2$.

12. Summary

John's isotherm has been applied to determine many parameters of finely divided and porous materials. By means of adsorption separation factor from binary mixture, surface area from surface energy, categorisation of micropores etc. have been determined. Deduction of more than half a dozen well known isotherms from John's isotherm using only minor reasonable approximations show that John's isotherm is fundamentally a practical and useful isotherm.

13. Appendix

a	Amount adsorbed
l	Langmuir constant
C_o	A constant in John's isotherm (solute adsorption)
C	A constant in John's isotherm. Intercept of isotherm from plot $\log\log p = C + m \log v$
c	Concentration
D	A constant in Dubinin equation
m	A constant in Dubinin equation
n	A constant in John's isotherm
p	Pressure
p^o	Saturation pressure
T	Temperature
V	Molar volume
v	Volume adsorbed at pressure p
v^o	Volume adsorbed at saturation pressure p^o
v_v	Molar volume of adsorbate at experimental temperature
V_f	Molar volume of adsorbate fluid at experimental temperature
V_{v12}	$V_{v1}Y_1 + V_{v2}Y_2$
V_{f12}	$V_{f1}Y_1 + V_{f2}Y_2$
γ_{12}	$\gamma_1 Y_1 + \gamma_2 Y_2$
x_1	Adsorbed mole fraction of gas 1
x_2	Adsorbed mole fraction of gas 2
Y_1	Mole fraction of gas 1
Y_2	Mole fraction of gas 2
c_1	A constant in John's isotherm
c_2	A constant in John's isotherm

References

1. P. T. JOHN and J. N. BOHRA, *Indian J. Technol.* **8** (1970) 34.
2. P. T. JOHN, D. K. SURI and K. C. NAGPAL, *J. Mat. Sci.* **20** (1985) 2071.
3. P. T. JOHN, V. G. CHETTY and K. K. DATTA, *Carbon* **15** (1977) 169. Errata, *Carbon* **16** (1978) 79.
4. P. T. JOHN, D. K. SURI, K. C. NAGPAL and T. A. K. GHORI, *J. Sci. & Indus. Research* **40** (1981) 373.
5. K. C. NAGPAL and P. T. JOHN, *Carbon* **16** (1978) 359.
6. S. BRUNAUER, "The Adsorption of Gases and Vapours," (Princeton University Press, Princeton, 1943).
7. G. JURA, W. D. HARKINS and E. H. LOESER, *J. Chem. Phys.* **14** (1946) 344.
8. Y. FU and F. E. BARTELL, *J. Phys. & Colloid Chem.* **55** (1951) 662.
9. G. L. MADAN, M. M. PATEL and H. C. SRIVASTAVA, *Indian J. Textile Technol.* **1** (1976) 9.
10. P. T. JOHN and J. N. BOHRA, in Proc. of the 21st Biennial Conf. on Carbon, 1993.
11. P. T. JOHN, D. K. SURI and K. C. NAGPAL, in Proc. 19th Biennial Conf. on Carbon, 1989, p. 15.
12. *Idem.*, *J. Mat. Sci.* **11** (1992) 956.
13. W. K. LEWIS, B. GILLILAND, B. CHERLOW and W. P. CADOGAN, *Ind. Eng Chem.* **42** (1950) 1619.
14. I. REICH, *J. Colloid Sci.* **14** (1951) 562.
15. P. T. JOHN and R. K. AGGARWAL, *Indian J. Technol.* **14** (1976) 139.
16. P. T. JOHN, *ibid.* **2** (1988) 141.
17. P. T. JOHN, D. K. SURI, S. S. SINGHAL, *Carbon* and K. C. NAGPAL, *Carbon* **27** (1989) 547.
18. P. T. JOHN, *Carbon* **22** (1984) 559.
19. P. T. JOHN and J. N. BOHRA, *Indian J. Technol.* **30** (1992) 531.
20. P. T. JOHN, *ibid.* **27** (1989) 547.
21. J. T. NALAN, T. W. McKEEHAN and R. F. DANNER, *J. Chem. Engg. Data* **26** (1981) 112.

22. R. F. DANNER and L. A. WENZAL, *A.I.C.H.E.J.* **15** (1969) 515.
23. P. T. JOHN, R. K. SURI and K. C. NAGPAL, *Carbon* **22** (1984) 575.
24. A. S. KUNJU, Ph.D. thesis, University of Kerala, 1989. p. 73.
25. A. S. VOYUTSKY, Colloid Chemistry, Mir Publishers, Moscow, 1978.
26. V. KIREEV, Physical Chemistry, Higher School Publishing House, Moscow, 1988.
27. V. S. ACHARI and T. S. ANIRUDHAN, *Indian J. Chem. Technol.* **2** (1995) 137.
28. V. S. ACHARI, Ph.D. thesis. University of Kerala, 1998. p. 124.

Received 28 December 1999
and accepted 10 August 2000