Monolayer and Specific Surface Area Computations for Fourteen Organic Vapour-Charcoal Systems

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Summary: Monolayer and specific surface area values have been reported for fourteen different organic vapours adsorbed on charcoal. Five well known equations namely Langmuir. Joyner, Kaganer, Reciprocal pressure - volume and BET were employed using IBM 360 - G44 computer programme for computations. Comparison of Joyner and BET monolayer values is given for four organic compounds whilst monolayer and specific surface area values are reported and discussed for fourteen organic compounds adsorbed on charcoal.

Introduction

BET method using physical adsorption has extensively been used for the measurement of specific surface area of solids [1]. The literature contains surface area values obtained by this method in abundance. Other equations used for the surface area measurement are the Langmuir, the Joyner (a modified BET equation), the Kaganer and the reciprocal pressure - volume. These have not been as frequently used as the BET equation. In this paper, we have used all the above equations to calculate monolayer capacities employing IBM 360/G-44 computer programme. These values have been compared keeping in mind the assumptions involved in the derivation of these equations. The BET and Joyner computed values [2] have been listed for various n values. Other useful comparative monolayer capacity studies have been reported by De Boer and Klemperer and Gottwald [3]. Similar studies have been reported by Ross [4] for BET and Hutig equations. Joyner [5] et al. have shown the application of the BET general equation after modifying it to a suitable form and has found good agreement between the calculated and experimental isotherms upto 0.8 relative pressures.

Isotherms lead to the quantitative evaluation of monolayer capacity of an absorbate. This determination is important, not only industrially, but also in understanding the nature of adsorption. The main aim of the present study is two fold. First to evaluate monolayer capacities at different temperatures of some organic vapours using Joyner plots with variation in n values thus comparing the results with standard BET data. Second to evaluate and report monolayer capacities of fourteen different compounds adsorbed on the same adsorbant (charcoal) by different available methods.

Computation and Results

The monolayer capacity values were computed on analytical computing system IBM/360/G-44 by using local programme. The incorporated equations are well known [5,6] and are left out for lack of space and risk of repetition. The values of saturation vapour pressures are adopted from literature [7]. For Joyner equation the n values were varied from 1 to 2 in intervals of 0.25 and the functions ϕ and θ were calculated. Plots were drawn between the corresponding functions and Vm were

calculated taking only the linear portions of these plots. The calculations are carried out on data given in reference 8, on the adsorption isotherms of methyl acetate, dimethyl ketone, diethyl ether and 1,2-dichloroethane. The underlined values indicate that straight lines were obtained in the plots for individual values of n. The values of Vm obtained at different temperatures and for different n values are produced in table I through IV for various organic vapours on coconut shell charcoal.

Vm values in $_{cc}\ g^{-1}$ at O°C calculated by Joyner, Langmuir, Kaganer and RPV-method are given in table V. These computations have been done on adsorption isotherms data pertaining to the adsorption of methyl acetate, ethyl formate, ethyl acetate, methyl propionate, n-propyl acetate, dimethyl ketone, methyl ethyl ketone and diethyl ketone, dimethyl ether, diethyl ether and dipropyl ether, and 1,1-dichloroethane, 1,2-dichloroethane and 1,2-dichloropropane on coconut shell charcoal. Additional results are given in table VI and VII.

Discussion

1. Monolayer Capacity

Table I through IV contain Joyner's Vm values for four organic compounds calculated at different temperatures and n values along with Vm values calculated by BET equation. The underlined values indicate that the best straight line was obtained for these n values. The BET values for Vm are very low specially at lower temperature, the greatest difference is 39% for methyl acetate at 40°C. However this difference decreases with increase of temperature from values for n = 1. The difference between BET values and the underlined Joyner values ranges between 0-24%. Similarly the disagreement among these values is greatest at lower

Table-I (METHYL ACETATE)

Monolayer capacities (V_m) of coconut shell Charcoal for methyl acetate at different temperatures

	Joyner Plots					BET	BET
Temperature	1.0	1.25	1.5	1.75	2.0	Plot	Range
0.00 C	117.96	110.09	99.04	89.93	82.38	75.89	(0.0-0.3)
40.00	110.55	98.24	88.66	81.20	75.01	67.35	(0.0-0.3)
57.10	102.82	93.13	85.54	79.47	74.48	63.89	(0.0-0.3)
99.71	85.60	81.81	79.36	77.71	76.69	75.28	
136.46	77.21	75.04	73.66	73.20	72.85	74.32	

Table-II (DIMETHYL KETONE)

Monolayer Capacities (V_m)of Coconut Shell Charcoal for Dimethyl Ketone at different temperatures.

Temperature	Joyner Plots					BET
°C	1.0	1.25	1.5	1.75	2.0	Plot
O.O	109.19	108.45	97.97	89.44	82.39	88.03
40.0	119.13	106.37	96.55	88.79	82.40	94.34
56.3	104.95	97.22	91.49	87.11	83.75	79.20
99.48	95.30	90.58	97.57	85.61	84.37	81.57
138.27	83.52	80.21	78.30	77.19	76.53	74.48
183.10	68.37	66.23	65.27	64.79	64.58	64.45

Table-III (DIETHYL ETHER)

Monolayer capacities (V_m) of Coconut Shell Charcoal for Diethyl Ether at different temperatures

Temperature	Joyner Plots					BET Plot	BET Plot
°C	1.0	1.25	1.5	1.75	2.0		
O.O	93.94	84.03	75.57	68.66	62.96	61.96	(0-0.3)
34.60	85.5	79.36	71.17	64.84	60.28	54.43	(0.07-0.28)
40.00	80.21	73.72	68.67	64.68	61.47	56.58	(0.0-0.27)
99.60	64.54	62.89	61.89	61.32	61.00	59.0	
138.80	58.47	56.74	55.80	55.19	54.87	53.60	
183.10	48.03	57.52	47.39	47.27	47.27	47.37	

Table-IV (1,2-DICHLORO ETHANE)

Monolayer capacities (V_m) of Coconut Shell Charcoal for 1,2-Dichloroethane at different temperatures

Temperature	Joyner Plots					BET	BET
°C	1.0	1.25	1.5	1.75	2.0	Plot	Range
O.O	116.84	103.24	92.76	84.40	77.65	78.47	(0-0.27)
40.0	113.79	99.14	89.28	81.19	74.51	89.65	(0-0.11)
63.96	94.27	87.23	81.90	77.77	74.55	76.39	(0.003-0.13)
79.45	91.62	86.66	83.25	80.85	79.20	79.48	(0.02-0.1)
99.48	89.48	84.54	81.06	78.56	76.75	74.29	(0.015-0.14)
136.20	82.46	79.03	77.58	76.72	75.88	76.66	(0.003-0.06)

Table-V: V_m values at 0°C calculated by various methods.

Vapour	V_m(cc g^{-1})			
	Joyner	Langmuir	Kaganer	RPV
Methyl Acetate	117.96	119.59	110.92	114.29
Ethyl Formate	111.78	111.94	105.93	99.66
Ethyl Acetate	90.05	91.87	87.10	90.91
Methyl Propionate	89.91	92.94	89.13	86.96
n-Propyl Acetate	74.55	78.32	76.91	78.00
Dimethyl Ketone	109.19	111.66	110.28	111.11
Methyl Ethyl Ketone	103.19	103.19	100.00	101.01
Diethyl Ketone	92.79	92.85	93.33	92.59
Dimethyl Ether	128.81	128.77	131.83	125.00
Diethyl Ether	93.94	93.95	89.13	90.91
Dipropyl Ether	71.04	71.04	69.58	74.07
1,1-Dichloro Ethane	108.61	113.20	107.15	114.29
1,2-Dichloro Ethane	111.05	114.05	110.92	117.65
1,2-Dichloro Propane	93.81	99.07	100.00	-

Table-VII: Values of C constant calculated from Joyner and Langmuir equations.

Vapour	C_{Joyner}	$C_{Langmuir}$
Methyl Acetate	59.08	50.44
Ethyl Formate	75.28	72.58
Ethyl Acetate	87.27	87.54
Methyl Propionate	89.91	93.20
n-Propyl Acetate	38.54	36.51
Dimethyl Ketone	93.52	119.40
Methyl Ethyl Ketone	61.51	61.33
Diethyl Ketone	44.38	43.97
Dimethyl Ether	116.37	116.36
Diethyl Ether	59.6	59.64
Dipropyl Ether	43.91	43.12
1,1-Dichloro Ethane	96.78	67.65
1,2-Dichloro Ethane	49.66	51.33
1,2-Dichloro Propane	31.79	33.21

temperature which idicates the weakening of adsorbate adsorbent interaction at higher layers and perhaps due to non-localized adsorption the saturation of monolayer capacity is reached quicker at higher temperatures.

The irregular change in Vm values of BET equation with increase in temperature is however misleading [9] and it is difficult to arrive at any logical conclusion except that this equation is not suitable for calculation of Vm especially when n values are very close to unity. This seems to be true for these adsorbates as the n values are below 2 in most cases.

Another prominent difference among the BET and Joyner values is that the BET values are always lower than Joyner values. This has been explained in a derivation carried out by Hill [10] where it has been shown that when sufficient adsorption has occurred to cover the surface with exactly one layer of molecules the fraction of surface θ_0, not covered by any molecule is dependent on the BET C value and is given by

$$\theta_0 = \frac{C^{\frac{1}{2}} - 1}{C-1}$$

From the above equation it is evident that when sufficient adsorption has occurred to form a monolayer there is still always some fraction of surface unoccupied.

Indeed, only for C values approaching infinity will θ_0 approach zero and in such cases the high adsorbate-surface interaction can only result from chemisorption. For nominal C values, say near 100, the fraction of surface unoccupied when exactly sufficient adsorption has occurred to form a monolayer is 0.91. Therefore, on the average each occupied site contains about 1.1 molecules. The implication here is that the BET equation indicates the weight of adsorbate required to

Table-VI: Monolayer capacities (V_m) at different temperatures calculated by Langmuir equation

Vapour	V_m (Temperature)
Methyl Acetate	109.22(40.00);103.83(50.10);87.46(99.71); 75.30(139.46).
Ethyl Formate	105.84(40.00);99.62 (100.16)
Ethyl Acetate	91.71(40.00);77.28(76.06);68.90(99.48); 62.16(139.48);55.78(180.53).
Methyl Propionate	92.40(40.00);73.78(79.85); 70.20(99.88); 59.95 (138.73)
n-Propyl Acetate	74.34(40.00);59.39(99.54); 53.41(139.53); 43.70(181.54).
Dimethyl Ketone	118.62(40.00);107.22(56.3); 97.11(99.48); 79.01(138.27); 59.67 (183.10).
Methyl Ethyl Ketone	93.64(50.00);83.76(79.5);71.44(139.15); 63.05(181.20)
Diethyl Ketone	85.53(50.00);70.91 (99.4);62.48(139.09); 51.90(182.4)
Dimethyl Ether	83.24(50.00);61.86(99.00);51.21 (139.41); 44.71(182.64)
Diethyl Ether	84.25(34.6);80.77 (40.00);66.20 (99.65); 57.92(138.85);49.75(183.14).
Dipropyl Ether	67.77(50.00);51.35(99.66);46.66(139.55); 140.88(181.00).
1,1-Dichloro Ethane	98.63(40.00);93.90(64.00);90.82(79.50); 85.52(99.59;70.63(136.65)
1,2-Dichloro Ethane	113.75(40.00);94.04(63.96);93.77(79.45); 89.47(99.48).
1,2-Dichloro Propane	92.09(40.00);80.72(63.88); 76.75(79.20); 73.01(99.22);60.17(136.20).

*V_m values at different temperatures (bracketed)

Table-VIII: Specific Surface Areas (A_m) Calculated for 50% Activated Coconut Shell Charcoal by Using Langmuir Monolayer Capacities.

Vapour	ρ(O°C)	$mX10^{-16}(A)^2$	t°C	$A_m(m^2g^{-1})$	
Methyl Acetate	0.95932	27.75	(23.49)	892.71	(755.34)*
Ethyl Formate	0.9117	28.70	(25.17)	864.21	(757.92)
Ethyl Acetate	0.92454	31.44	(28.77)	776.98	(710.99)
Methyl Propionate	0.93871	31.60	(37.85)	790.03	(946.31)
n-Propyl Acetate	0.90835	35.64	(35.8)	750.87	(783.90)
Dimethyl Ketone	0.81248	26.35	(16.17)	791.58	(485.69)
Methyl Ethyl Ketone	0.82551	30.12	(24.58)	836.07	(682.38)
Diethyl Ketone	0.8337	33.69	(31.17)	841.46	(778.52)
Dimethyl Ether	0.6905	25.17	(14.47)	871.87	(501.23)
Diethyl Ether	0.73629	33.12	(30.07)	837.03	(759.95)
Dipropyl Ether	0.76611	39.94	(45.64)	763.23	(872.17)
1,1-Dichloro Ethane	1.2049	28.91	(19.11)	859.11	(558.32)
1,2-Dichloro Ethane	1.28248	27.733	(30.31)	886.97	(905.43)

*A_m values calculated from Covalent and Vadner Waals radii [17].

form a monolayer on the surface, although no such phenomenon as a uniform monolayer exists in the case of physical adsorption.

The Joyner equation is more accurate in calculations of Vm values for microporous adsorbants, like charcoals, than BET equation, because of its three parameter nature. Furthermore, BET equation gives inaccurate values [11] of Vm especially when C values are less than 100. This reasoning seems to be true in this case also, as the C values are less than 100 for most of the adsorbates as given in our earlier results [6]. The change in Vm values for different n values is more at lower temperatures than at higher temperatures. This term indicates the quick attainment of equilibrium between rates of condensation and evaporation.

The computed monolayer capacity value for other equations are given in table V and VI. In table V, the quantitative agreement between these values is quite reasonable and it validates a direct use of all the four methods for the calculation of V_m. The

averaged limiting values of relative pressures range from 0.01 to 0.46 for Kaganer method and 0.006 to 0.46 for reciprocal pressure volume method. From the knowledge of adsorption processes, it appears probably that the attractive forces act largely through the active atoms or group of atoms, viz., carbonyl group in esters and ketones, oxygen in ethers and chlorine in dichloro hydrocarbons. Therefore, we expect a packing of the molecules with their long axes perpendicular to the surface of the adsorbent and the contact point is attained through these active atomic groups. However, the possibility of adsorption of molecules with their long axes parallel to the surface of the adsorbent cannot be ruled out within limits, because the V_m values do decrease with increase in the lengths of the molecules in the same homologous series. A mixed mode of adsorption is therefore, envisaged as is clear from the nearly same V_m values for 1,1-dichloro ethane and 1, 2-dichloro ethane.

BET equation for the limiting situation when $n = \infty$ was also used to calculate V_m values but these values showed poor agreement with the V_m values obtained from Langmuir and Joyner equations. In most of the systems the plots were non-linear with respect to zero degree temperature. However, the V_m values from isotherm at higher temperatures were reasonably comparable within the errors limits.

Table VII embodies the values of constant C which is related to the heat of adsorption of the monolayer. Usually C values are linearly related to the heat of adsorption of the monolayer. The highest C value is for dimethyl ether and the lowest is for n-propyl acetate.

2. Specific surface area

In table VII, values for specific surface area calculated for individual adsorbates at O°C have evaluated using the relationship [12].

$$A_m = 0.269\ \sigma_m \cdot V_m \quad (1)$$

where A_m, V_m and σ_m are the specific surface area of the adsorbent, monolayer capacity and the cross sectional area of the adsorbed molecule respectively. The calculation of σ_m was carried out using the equation [13].

$$\sigma_m = 1.091\ (M/N\rho)^{2/3} \quad (2)$$

for spherical shaped hexagonal close packing for the adsorbed molecules and using densities of their liquid states. In equation (2), M N and ρ are molecular weight, Avogardo's number and the density of the adsorbate assumed to be present in liquid state, respectively. However, in great many cases this assumption is not justifiable, and in majority of such cases the σ_m values are calculated by assuming the orientation of the long axis of the adsorbed molecule to be parallel to the surface of the adsorbent. The packing factor value (1.091) was also changed because of loose packing of the molecules.

The average surface area, A_m, (calculated by using cross-sectional areas of organic vapours which in turn were obtained from liquid density values) is 830.01 $m^2\ g^{-1}$, with average deviation value 38.4 $m^2\ g^{-1}$ (4.6%) and the maximum and minimum deviations are 66.8 $m^2\ g^{-1}$ (8.0%) and 6.06 $m^2\ g^{-1}$ (0.7%). These values are almost identical with those obtained by

Brunauer and Emmett [14] as : A_m= 829 m^2 g^{-1};average dev. 29 m^2 g^{-1} (3.5%) and max. dev. 65.0 m^2 g^{-1} (7.8%). In earlier reports [15,16] the extreme values for specific surface areas of coconut charcoal obtained from nitrogen gas adsorption are 1375 m^2 g^{-1} and 644 m^2 g^{-1}. In fact these values are indicative of a proportional extent of activation to which a particular charcoal sample has been treated. Our computed average value of 830.01 m^2 g^{-1} confirms that the sample under investigation corresponds to a 50% activation state as affirmed by Pearce [17]. Further, this value is also quite close to 895 m^2 g^{-1} for nitrogen and 829 m^2 g^{-1} for methane adsorbed on sample [16]. The overall consistancy in the values of surface areas also indicates that there are no pores of narrow-neck or ink bottle shape on the surface of the charcoal, but instead the pore size is large enough to accomodate the large adsorbate molecules. Such behaviour has been previously by reported by Tsurvizumi [18] for carboxylic acids on silica gel.

σ_m values have also been calculated from covalent and van der Walls radii [19] of atoms (hydrogen atoms not included in calculations). Here the molecular orientation at the surface of the solid is assumed to be parallel with its long chain axis and the closest approach between the absorbate molecules is 6.2 $\mathring{A}$. These calculations have been included in column 4 of Table VIII. The last column of this table contains the surface area values obtained by using these σ_m values.

The surface area values calculated in this way are lower and vary considerably as compared with those obtained from liquid density σ_m values. Surface areas obtained with dimethyl ketone, dimethyl ether and 1,1-dichloroethane are very low, indicating the roughness factor of about 1,5 for these vapours.

These calculations, however, demonstrate that the effective area of an adsorbed molecule is quite different from its actual cross-sectional area. Although the present study affords a comparative quantitative outlook onto the nature of the adsorption process, further work comprising of the computation of some of the thermodynamic functions would be much revealing in order to have a clear exposition on molecular level of the process of adsorption.

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