

Computer Genrated Monolayer Capacities and Specific Surface Areas of Charcoal Using Organic Vapours as Absorbates

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Summary: Computer generated monolayer capacity values and surface area values are reported for fourteen different compounds, adsorbed on charcoal. These values are obtained using Langmuir, Joyner, Kaganer and Reciprocal-pressure-volume equations on a IBM 360/G-44 Computer programme. Our surface area and monolayer capacity values differ from the well known BET values; an explanation for which is given.

Introduction

BET method using physical adsorption has extensively been used for the measurement of specific surface area of solids⁽¹⁾. The literature contained in abundance surface area values obtained by this method. There are numerous other equations like the Langmuir, the Joyner, the Kaganer and the Reciprocal pressure-volume, which have not been used as frequently as the BET equation. We have made use of the last mentioned equations to calculate monolayer capacities and surface areas by employing IBM 360/G-44 computer programme. The BET surface area values are not included in the results reported here.

Isotherms have been successfully used to get quantitative informations about the nature of adsorbent surface and its porosity as a function of mode of packing of the adsorbate molecules. Specific surface areas are normally studied by making use of adsorption isotherms leading to a quantitative evaluation of monolayer capacity of an adsorbate. This determination is important, not only industrially, but also in understanding the nature of adsorption, through calculations of specific surface area and various thermodynamic functions. The main aim of the present study is to evaluate in the first instance, monolayer capacities of fourteen different compounds adsorbed on the same adsorbent (charcoal) by different available methods and secondly, to calculate the specific surface area of the adsorbent. A clear exposition as to the determination of thermodynamic functions has already been given in earlier work⁽²⁾.

Computational Procedure: Various methods for the evaluation of monolayer capacities are available which can be advantageously used for the computation of

specific surface areas of adsorbents covering an entire range of relative pressures. These include the Langmuir⁽³⁾, the point B⁽⁴⁾ and the Joyner method⁽⁵⁾. On the other hand method like Kaganer's Reciprocal Pressure-Volume and the BET method are applicable to a certain range of relative pressures and usually the results obtained are lower as compared with those just cited in first category of methods.

The monolayer capacity values were computed on analytical computing system IBM 360/G-44 by using local programmes. The values for saturation vapour pressures are adopted from literature⁽⁶⁾ and the specific surface area was calculated for individual adsorbates at 0°C by use of the relationship⁽⁷⁾.

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

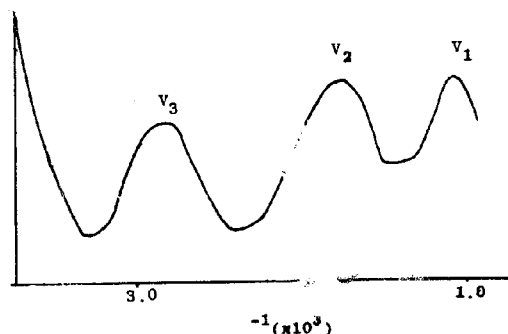
where A_m , V_m and σ_m are the specific surface area of the adsorbent, monolayer capacity and the cross sectional area of the adsorbed molecule respectively. The calculation of σ_m was carried out using the equation⁽⁸⁾.

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

for spherical shaped and hexagonal close packing for the adsorbed molecules and using densities of their liquid states. In equation (2), M , N and ρ are the molecular weight, Avogadro'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 σ_m values are calculated by assuming the orientation of the long axis

Table 1. Analytical data for amminenickel(II) halides and pseudohalides

Compound	Found (%)					Calculated (%)						
	Ni	C	N	H	X	NH ₃	Ni	C	N	H	X	NH ₃
Ni(NH ₃) ₄ (NCS) ₂	24.33	9.78	34.55	4.80		27.82	24.17	9.88	34.58	4.94		27.99
Ni(NH ₃) ₂ (NCS) ₂	28.41	11.30	26.71	3.58		16.45	28.10	11.49	26.81	3.87		16.28
Ni(NH ₃) ₆ Br ₂					49.52	31.50					49.86	31.80
Ni(NH ₃) ₂ Br ₂					62.96	13.18					63.29	13.46
Ni(NH ₃) ₆ I ₂					61.02	24.38					61.23	24.61
Ni(NH ₃) ₂ I ₂					73.25	9.54					73.25	9.81

Fig. 2 : Electronic spectrum of [Ni(NH₃)₆]²⁺Table 2: 10Dq values (cm⁻¹) for octahedral Ni²⁺ with various ligands.

	Ni(NH ₃) ₆ X ₂	Ni(NH ₃) ₄ X ₂	Ni(NH ₃) ₂ X ₂	NiX ₂
X=Br ⁻	11000	—	7800	6200
X=I ⁻	10900	—	7600	5950
X=NCS ⁻	—	10800	10200	9600

Results and Discussion

Energies of the $3A_{2g} \rightarrow 3T_{2g}$ band (equivalent to 10Dq) as determined from the electronic spectra of the amminenickel(II) complexes are summarised in Table 2. Additional calculated 10Dq values for NiBr₂, NiI₂ and Ni(NCS)₂ (or [Ni(NCS)₆]⁴⁻) using Jorgensen's method are included.

The following 10Dq values are reported in the literature: [Ni(NH₃)₆]²⁺, 10750 cm⁻¹ (4); NiBr₂, 6800 cm⁻¹ (6); [Ni(NCS)₆]⁴⁻, 9600 cm⁻¹ (11); Ni(NCS)₂, 9600 cm⁻¹ (7).

No literature value is available for NiI₂ (presumably the bulky iodide ion is ill-suited for six co-ordination). There is reasonable agreement between literature values and those obtained in this work; some of the calculated NiX₂ 10Dq values may show significant differences and this is partly attributable to departures from perfect octahedral geometry. On the basis of this work, the spectrochemical series for the ligands is arranged thus: NH₃ > NCS⁻ > Br⁻ > I⁻.

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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 computations were done on adsorption isotherm 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⁽⁹⁾, dimethyl ether, diethyl ether, and dipropyl ether⁽¹⁰⁾, and 1,1-dichloro-ethane, 1,2-dichloro ethane and 1,2-dichloro propane⁽¹¹⁾ on coconut shell charcoal. the results of these calculations are reported in Table I through IV. A brief treatment on the mode of packing during adsorption has been given at the end of discussion.

Discussion:

The computed monolayer capacity (V_m) values are tabulated in Table I and II. In Table I 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 probable 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 III 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⁽⁴⁾. The highest C value is for dimethyl ether and the lowest is for n-propyl acetate.

The average surface area, A_m , (calculated by using

Table 1. 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 2. Monolayer capacities (V_m) at different temperatures ($^{\circ}\text{C}$) calculated by Langmuir equation.

Vapour	V_m (Temperature)
Methyl acetate	*109.22 (40.); 103.83 (57.10); 87.46 (99.71); 75.30 (139.46).
Ethyl Formate	105.84 (40.); 99.62 (100.16).
Ethyl Acetate	91.71 (40.); 77.28 (76.06). 68.90 (99.48); 62.16 (139.48); 55.78 (180.53).
Methyl Propionate	92.40 (40.); 73.78 (79.85); 70.20 (99.88); 59.95 (138.73).
N-Propyl Acetate	74.34 (40.); 59.39 (99.54); 53.41 (139.53); 43.70 (181.54).
Dimethyl Ketone	118.62 (40.); 107.22 (56.3); 97.11 (99.48); 79.01 (138.27); 59.67 (183.10).
Methyl Ethyl Ketone	93.64 (50.); 83.76 (79.5); 71.44 (139.15); 63.05 (181.20).
Diethyl Ketone	85.53 (40.); 70.91 (99.4); 62.48 (139.09); 51.90 (182.4).
Dimethyl Ether	83.24 (50.); 61.86 (99.); 51.21 (139.41); 44.71 (182.64).
Diethyl Ether	84.25 (34.6); 80.77 (40.); 66.20 (99.65); 57.92 (138.85); 49.75 (183.14).
Dipropyl Ether	67.77 (50.); 51.35 (99.); 46.66 (139.); 40.88 (181.).
1,1-Dichloro Ethane	98.73 (40.); 93.90 (64.) 90.82 (79.50); 85.52 (99.50); 70.63 (136.65).
1,2-Dichloro Ethane	113.75 (40.) 94.04 (63.96); 93.77 (79.45); 89.47 (99.48).
1,2-Dichloro Propane	92.90 (40.); 80.72 (63.88); 76.75 (79.20);

cross-sectional areas of organic vapours which in turn were obtained from liquid density values) is $830.01 \text{ m}^2 \text{ g}^{-1}$, with average deviation value $38.4 \text{ m}^2 \text{ g}^{-1}$ (4.6%) and the maximum and minimum deviations are $66.8 \text{ m}^2 \text{ g}^{-1}$ (8.0%) and $6.06 \text{ m}^2 \text{ g}^{-1}$ (0.7%). These values are almost identical with those obtained by Brunauer and Emmett⁽¹²⁾ as : $A_m = 829 \text{ m}^2 \text{ g}^{-1}$; average dev. $29 \text{ m}^2 \text{ g}^{-1}$ (3.5%) and max. dev. $65.0 \text{ m}^2 \text{ g}^{-1}$ (7.8%). In earlier reports^(13,14) the extreme values for Specific surface areas of coconut charcoal obtained from nitrogen gas adsorption are $1375 \text{ m}^2 \text{ g}^{-1}$ and $644 \text{ m}^2 \text{ g}^{-1}$. 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 $830.01 \text{ m}^2 \text{ g}^{-1}$ confirms that the sample under investigation corresponds to a 50% activation state as affirmed by Pearce⁽¹⁵⁾. Further, this value is also quite

close to $895 \text{ m}^2 \text{ g}^{-1}$ for nitrogen and $829 \text{ m}^2 \text{ g}^{-1}$ for methane adsorbed on sample¹⁴. The overall consistency 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 accommodate the large adsorbate molecules. Such behaviour has been previously reported by Tsurvizi⁽¹⁶⁾ for carboxylic acids on silica gel.

σ_m values have also been calculated from covalent and van der Waals radii⁽¹⁷⁾ 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 adsorbate molecules is 6.2 \AA . These calculations have been included in column 4 of Table IV. The last column of this table contains the surface area values obtained by using these σ_m values.

Table 3. 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-DichloroEthane	49.66	51.33
1,2-Dichloro Propane	31.79	33.21

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 ketones, 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 comparing 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.

The observation that the BET surface area values are lower than the values given here may be explained in terms of a derivation carried out by Hill⁽¹⁸⁾. It has been shown by Hill that when sufficient adsorption has occurred to cover the surface with exactly one layer of molecules the fraction of surface, θ_o , not covered by any molecule is dependent on the BET C value and is given by

$$\theta_o = \frac{C^{1/2} - 1}{C - 1}$$

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_o 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 0.091. Therefore, on the average each occupied site contains about 1.1 molecules. The implication here is that the BET equa-

Table 4. Specific Surface Areas (A_m) Calculated for 50% Activated Coconut Shell Charcoal by Using Langmuir Monolayer Capacities.

Vapour	ρ (0°C)	$\sigma_m \times 10^{-16}$ (A) ²	t°C	A_m (m ² g ⁻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 Vander Waals radii¹⁷

tion indicates the weight of adsorbate required to form a monolayer on the surface, although no such phenomenon as a uniform monolayer exists in the case of physical adsorption.

Finally a word may be said on the orientation of adsorbed molecules onto the solid and their mode of packing. A symmetric or a small molecule, with a small side chain, would have its polarity transmitted to its nearest ends and hence is seen to adsorb with its entire body parallel to the surface. This would lead to large values of specific surface areas as is found to be the case for methyl acetate, ethyl formate, dimethyl ether and dimethyl ketone. On the other hand a larger molecule, with a long side chain may easily be divided into its polar and non-polar ends. On adsorption, the molecules will therefore, stand erect with their polar groups attached to the surface. This enables them to pack together so as to make a monolayer on the surface and hence yield surface area values which lie on the lower side. The surface area values for methyl propionate, dipropyl ether and n-propyl acetate clearly bear this out. This effect hitherto has been observed for adsorption of long chain fatty acids on charcoal from aqueous solution¹⁹

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