Pakistan J. Sci. Ind. Res., Vol. 28, No. 3, June 1985

# MONOLAYER COMPUTED VALUES FOR THE ADSORPTION OF ORGANIC VAPOURS ON CHARCOAL USING JOYNER AND BET EQUATIONS

M. Afzal, J. Ahmed and P.K. Butt,

*Department of Chemistry, Quaid-i-Azam University, Islamabad*

(Received February 9, 1984; revised April 24, 1985)

The Joyner equation – a modified form of BET equation – has been used to compute monolayer values for the adsorption of organic vapours on coconut charcoal using the IBM-G44 Computer programme. BET and Joyner monolayer values have been compared at various temperatures together with n values between one and two.

## INTRODUCTION

Monolayer capacity values and surface area values computed through an IBM 360/G-44 computer programme were reported using the Langmuir, Joyner, Kaganer and Reciprocal pressure-volume equation [1]. The BET surface area and monolayer values were deliberately left out from an earlier publication [1] for future communication. The BET computed values are now compared with the Joyner values calculated through the Joyner equation obtained after modifying the BET equation for various n values [2].

Monolayer capacities ($V_m$) calculated through the BET and its modified Joyner equations have a limited range of relative pressure for their validity because the plots are usually linear within this range. For example, the BET equation plot is linear between 0.05 – 0.35 relative pressure limits [2]. Similar limits were observed for the Kaganer and reciprocal pressure volume methods [1].

Useful comparative studies have been undertaken by many workers to test these methods for calculating monolayer capacities. De Boer and Klemperer and Gottwald have compared BET method with Langmuir and DKG and have derived conclusive evidence of their interrelations [3]. Similar studies have been reported by Ross [4] for BET and Hutig equations. Joyner *et al* [5] have shown the application of the BET general equation after modifying it to a suitable form and have found good agreement between the calculated and experimental isotherms up to 0.8 relative pressures.

In the present study the monolayer capacity of activated coconut charcoal was determined by the BET and Joyner methods. An attempt has been made to compare these results and some useful conclusions have been drawn with respect to the use of both equations.

## PROCEDURE

Various functions involved in equations (3) and (5) were calculated on IBM-G44. For the Joyner equation the n values were varied from 1 to 2 in intervals of 0.25 and the functions $\phi$ and O were calculated. Plots were drawn between the corresponding functions and $V_m$ was calculated taking only the linear portions of these plots. The calculations with equation (2) were not included in the results as they were identical with the Langmuir values. The computations were carried out on data [6] of adsorption isotherm 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 $V_m$ obtained at different temperatures and for different n values are reproduced in Table 1 through 4 for various organic vapours on coconut shell charcoal.

## DISCUSSION

Tables 1-4 show the Joyner $V_m$ values for methyl acetate, dimethyl ketone, diethyl ether and 1,2-dichloroethane at different temperatures and n values along with $V_m$ values calculated by BET equation [3]. The underlined values indicate that the best straight line was obtained for these n values. The BET values for $V_m$ are very low, especially at lower temperatures. The greatest difference is 39% for methyl acetate at 40° However, this difference

Table 1. (Methyl acetate) monolayer capacities ($V_m$) of coconul shell charcoal for methyl acetate at different temperatures

| Temperature O°C | Joyner plots | | | | | BET plot | BET range |
|---|---|---|---|---|---|---|---|
| | 1.0 | 1.25 | 1.5 | 1.75 | 2.0 | | |
| 0.00 | 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 | 74.46 | 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 | 73.86 | 73.20 | 72.85 | 74.32 | |

Table 2. (Dimethyl ketone) monolayer capacities ($V_m$, of coconut shell charcoal for dimethyl ketone at different temperature

| Temperature O°C | Joyner plots | | | | | BET plot |
|---|---|---|---|---|---|---|
| | 1.0 | 1.25 | 1.5 | 1.75 | 2.0 | |
| 0.00 | 109.19 | 108.45 | 97.97 | 89.44 | 82.39 | 88.03 |
| 40.00 | 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 | 87.57 | 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 3. (Diethyl ether) Monolayer capacities ($V_m$) of coconut shell charcoal for diethyl ether at different temperatures

| Temperature O°C | Joyner plots | | | | | BET plot | BET range |
|---|---|---|---|---|---|---|---|
| | 1.0 | 1.25 | 1.5 | 1.75 | 2.0 | | |
| 0.00 | 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 | (0.47–0.28) |
| 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 | 59.00 | |
| 138.80 | 58.47 | 56.74 | 55.80 | 55.19 | 54.87 | 53.60 | |
| 183.10 | 48.03 | 47.52 | 47.39 | 47.27 | 47.27 | 47.37 | |

Table 4. (1,2-dichloro ethane) Monolayer capacities ($V_m$) of coconut shell charcoal for 1,2-dichloroethane at different temperatures

| Temperature | Joyner plots | | | | | BET | BET |
|---|---|---|---|---|---|---|---|
| 0$^{o}$C | 1.0 | 1.25 | 1.5 | 1.75 | 2.0 | plot | range |
| 0.00$^{o}$C | 111.05 | 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 | (0.15–0.14) |
| 136.20 | 82.46 | 79.03 | 77.58 | 76.72 | 75.88 | 76.66 | (0.003–0.06) |

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 the greatest at lower temperatures which indicates the weakening of adsorbate-adsorbent interaction at higher coverage and, as is often the case in non-localized adsorption, the saturation of monolayer capacity is reached quicker at higher temperatures.

The irregular change in $V_m$ values of BET equation with increase in temperature, at first sight, may appear misleading [7]. This may be explained by pointing out the evidence of the change of mode of packing as the temperature rises. It is known that small molecules whose polar and non-polar groups are in each other's vicinity, may transmit their polar nature to almost the entire molecule. This would make the molecule lie flat on the surface. On the contrary, a large molecule has well defined polar and non-polar ends (side-chains). Such molecules have a tendency to stand erect on the surface with their polar end attached to the surface. Thermal motions (two-dimensional translational, rotational and vibrational) change with temperature which may alter their orientations and mode of packing, thus changing their $V_m$ values.

Another prominent difference among the BET and Joyner values is that the BET values are always lower than the Joyner values. An explanation for such a behaviour has been earlier given by Afzal and Ahmad [1]. The limit of linearity of the plots of BET does not exceed 0.3 relative pressure value at lower temperatures. This certainly leads to the conclusion that certain fundamental factors have been omitted in this equation. Some of these factors have been discussed in the preceding paragraph.

The Joyner equation is more accurate (2) in calculations of $V_m$ values for microporous adsorbents, like charcoals than BET equation (3), because of its three parameter nature.

With C values less than $100^8$, the Joyner equation gives far more accurate $V_m$ values than the BET equation. It has been shown previously [1] that C values are related to the heat of adsorption of the monolayer and usually C values are linearly related to the heat of adsorption of the monolayer.

The change in $V_m$ values for different n values is more at lower temperature than at higher temperature. This term indicates the quick attainment of equilibrium between rates of condensation and evaporation.

## REFERENCES

1. M Afzal and Jamil Ahmed, J. Chem. Soc. Pakistan, **4**, 61 (1982).
2. S Brunauer, L.E. Copeland and D.L Kantro, *The Solid-Gas Interface* (Edward Arnold Ltd., London (1967), Chap. 3 ed. E.A. Flood, Vol. 1.
3. *Surface area determination,* eds, D.H Everett & R. H. Ottewill, Butterworths, London (1970) pp. 7, 55, 59.
4. S. Ross., J. Phys. Chem., **53**, 383 (1949).
5. L G. Joyner, E.B. Weinberger and C.W. Montgomery, J Am. Chem. Soc., **67**, 2182 (1945)
6. J.N. Pearce and A.C. Hanson, J. Phys. Chem., **39**, 679 (1935); J.N. Pearce and P.E. Peters, *Ibid.,* **42**, 229 (1938); J.N. Pearce and J.F. Eversole, *Ibid.,* **38**, 383 (1934).
7. S. Ross and J.P. Olivier, *On Physical Adsorption,* (Interscience Publishers, New York 1964), p. 196.
8. R.L. Bond (ed.), *Porous Carbon Solids,* (Academic Press, London 1967), Chap. I.