

Study of microporosity of active carbon spheres using inverse gas chromatographic and static adsorption techniques

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Abstract

Active carbon spheres (ACSs) with different porous structures prepared in the laboratory were characterized by static adsorption studies and inverse gas chromatographic (IGC) technique. Surface properties such as BET surface area, micropore volume and pore size in different regions of porosity were determined using different theoretical approaches. Thermodynamic parameters such as isosteric heat of adsorption, free energy of adsorption and dispersive component of the surface energy were determined using IGC technique from corrected retention volume of normal alkanes and corresponding branched alkanes. Thermodynamic parameters were used to assess the molecular sieving property of ACSs. It is observed that thermodynamic properties strongly depend on microporous character of ACSs. The variations observed in pore size determined by both of the techniques that is by static adsorption measurements and IGC may be attributed to the variation in analysis temperature, i.e. liquid N₂ temperature for adsorption studies and elevated temperature for IGC technique.

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1. Introduction

Porous adsorbents are usually characterized by studying the adsorption of various adsorbates in controlled conditions for the assessment of surface area and porosity [1]. Various empirical equations such as BET and Dubinin Radushkevich (DR) are used to analyze the adsorption data [2,3]. The DR method is especially used to assess the microporosity. In case of microporous solids, where filling of pores is the predominant mechanism of adsorption, the surface area is determined using conventional equilibrium adsorption measurements and theories are quite misleading. The situation in respect of assessment of pore size distribution (PSD) in micropore region (width < 20 Å) using adsorption data is also not very encouraging. The characteristic energy term of DR equation has been used by various authors [4,5] to give average pore size in the micropore region. The equations evolved for this purpose are again empirical in nature.

Nevertheless, in the absence of any other method for the assessment of average pore size in the micropore region, the use of these equations is getting wider acceptance.

There have been few attempts to use inverse gas chromatography (IGC) for assessment of surface properties of organic and inorganic materials which are strongly affected by nature of porosity [6–10]. The corrected retention volume of probes covering a size range is used to compute thermodynamic parameters such as isosteric heat of adsorption, free energy of adsorption and dispersive components of surface energy [11]. All types of interactions other than the ones which are dispersive in nature such as polar, acid/base interaction and hydrogen bonding can also be obtained using the IGC technique [11–14]. The interaction of polar probes and substrates involves dispersive as well as specific forces. Molecular sieving properties of microporous carbons are generally assessed by a molecular probe technique [15–17] apart from an IGC technique. An abrupt change in the values of thermodynamic properties assessed by IGC is a manifestation of molecular sieving effect. Hence, it is possible to ascertain pore size range by using IGC. However, it must be kept in mind that retention volume of a probe in case of gas–solid chromatography depends on kinetic effects also

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along with thermodynamics of adsorption. In case of microporous solids, the intragranular Knudsen diffusion followed by pore filling due to enhanced adsorption potential are predominant mechanism which lead to slow desorption of adsorbate molecules. Hence, it may not be correct to correlate changes in thermodynamic parameters to pore size only. Nevertheless, some interesting findings are reported in this paper, which suggest that the pore size determined by equilibrium adsorption and IGC measurements may correlate marginally.

In the present work, thermodynamic parameters mentioned above for probes such as n-alkanes and corresponding branched alkanes have been determined using IGC on microporous active carbons characterized using low temperature adsorption studies. An attempt has been made to correlate thermodynamic parameters with microporous structure of the adsorbent. The theory of the two methods is given in Section 3 of the paper in some detail.

2. Experimental

2.1. Materials

Active carbon spheres (ACSs), which have been used as stationary phase in GC columns in the present study, were prepared from a polymeric precursor, polystyrene sulfonate resin having 8 wt.% divinyl benzene copolymer in our laboratory. The particle size of the resin varied from 0.6 to 1.2 mm. The samples were prepared in a tubular quartz reactor of size (800 mm length \times 20 mm i.d.). The heating rate for all the samples was same, i.e. 1.8 K/min upto 393 K, 2.6 K/min upto 593 K and 3.6 K/min upto highest treatment temperature (HTT), i.e. 1123 K. Out of score of samples prepared under different sets of flow rates of activating agent CO₂ and duration of activation, three samples selected for present study were prepared as follows: The sample S₁ was prepared at CO₂ flow rate 20 ml/min and activation time 30 min, the sample S₂ was prepared at CO₂ flow rate 100 ml/min and activation duration 6 h and the preparation conditions of sample S₃ were, CO₂ flow rate 200 ml/min and activation time 20 h. The activation temperature was kept constant at 1123 K for all the three samples chosen for characterization by static and dynamic adsorption measurements. The particle size of final product obtained was in the range of 0.3–0.6 mm.

2.2. Gas adsorption measurements

Samples chosen for the present study were degassed at 523 K for 8 h under vacuum of 10⁻³ mmHg (1 mmHg = 133.322 Pa). Nitrogen adsorption isotherms of degassed samples were recorded in a static mode at 77 K using a Micromeritics 2375 surface area analyzer to characterize the porous texture of the ACS samples. Data obtained were analyzed using BET and DR equations for surface area and

micropore volume, respectively [1]. Additional information about pore size distributions were obtained using both the Horvath and Kawazoe [19] and BJH [20] methods for micro- and mesopores.

2.3. Gas chromatographic measurements

GC columns of stainless steel tube (15 cm \times 2 mm i.d.) were prepared using 0.1–0.5 g active carbon spheres as stationary phase. A dual column gas chromatograph 8610 Chemito, fitted with flame ionization detector, mass flow controller for carrier gas and Chemito 5000 data processor, was used for retention time measurements with precision of ± 0.01 min in the temperature range of 303–573 K. Columns were conditioned at 523 K for 10 h in a N₂ atmosphere at 30 ml/min flow rate. IOLAR (India) nitrogen was used as carrier gas at a flow rate ranging from 10 to 30 ml/min. A small volume of probe (less than 0.4 μ l) was injected in to the GC column with a 1 μ l Hamilton syringes. Retention volume and peak width of alkanes and corresponding branched alkanes recorded in the range of the flow rate variation were constant within a margin error of 5% showing the adsorption properties are independent of the measurement of flow rate. The retention volume was also independent of the amount of probe injected. Due to spherical shape of carbon particles and short length of the columns, the pressure drop in GC columns was negligible. Hence, inlet pressure was considered equal to the atmospheric pressure.

3. Results and discussion

3.1. Surface characteristics of carbons using static adsorption method

Adsorption isotherms obtained using N₂ as adsorbate at 77 K are generally used to characterize materials having molecular size pores. The three samples S₁, S₂ and S₃ selected for study showed wide range of surface properties as evident from the shape of adsorption isotherms given in Fig. 1. The isotherm of sample S₁ is of type I, whereas isotherms of samples S₂ and S₃ are the mixture of types I and IV reflecting micro- and mesoporous nature of activated carbons according to the BDDT classification [18]. The ascending pattern observed after the first point of inflection increases from sample S₁ to S₃. This may be due to widening of pores on increasing the duration of activation.

For assessment of microporosity, the DR equation [4] has been used.

$$W = W_0 \exp \left[- \left[RT \log \frac{(P_0/P)}{\beta E_0} \right]^2 \right] \quad (1)$$

where W_0 is the total volume of the micropores, W the volume that gets filled when the relative pressure approaches P/P_0 at temperature T (K), E_0 the characteristic adsorption

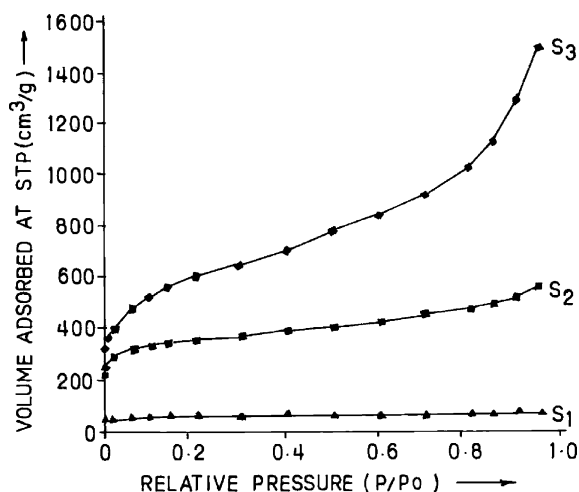


Fig. 1. N₂ adsorption isotherms of active carbon spheres at 77 K.

energy for a standard vapor, β the adsorbate affinity coefficient taken as 0.34 for nitrogen and R is the gas constant.

The DR plots between $\log W$ versus $\log^2(P_0/P)$ are shown in Fig. 2. The linear DR plots over a wide range of relative pressure indicate that a narrow micropore size distribution was present in all the ACS samples. This evidence is further confirmed by analysis of micropore size distribution by Horvath and Kawazoe method as shown in Fig. 3a. Isotherms of samples S₂ and S₃ show an upward deviation at high values of relative pressures, i.e. more adsorbate is adsorbed than expected. This 'excess' adsorption could be due to the filling of mesopores or multilayer adsorption on non-porous surface. The value of $\log W$ obtained by extrapolation of DR plot and y-axis intercept gives the micropore volume and the slope gives the adsorption energy E_0 in all cases.

According to Dubinin [4] pore width is inversely proportional to adsorption energy E_0 given by the equation:

$$\frac{d_D}{2} = \frac{12}{E_0} \quad (2)$$

where E_0 is in kJ/mol and d_D is the pore width in nm obtained by this relationship.

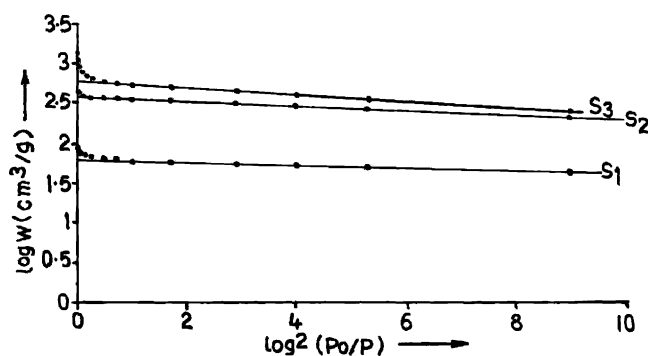
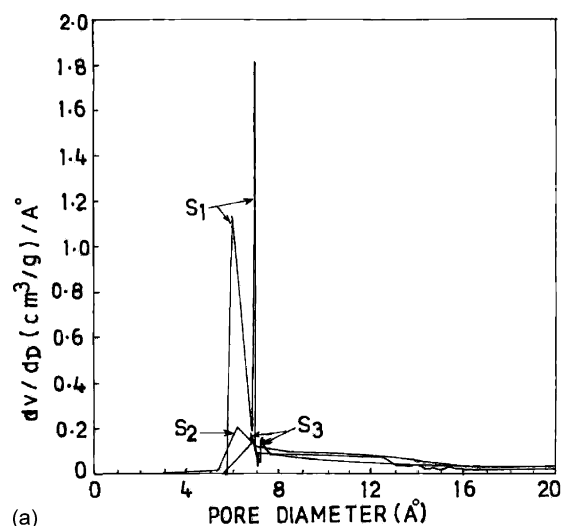
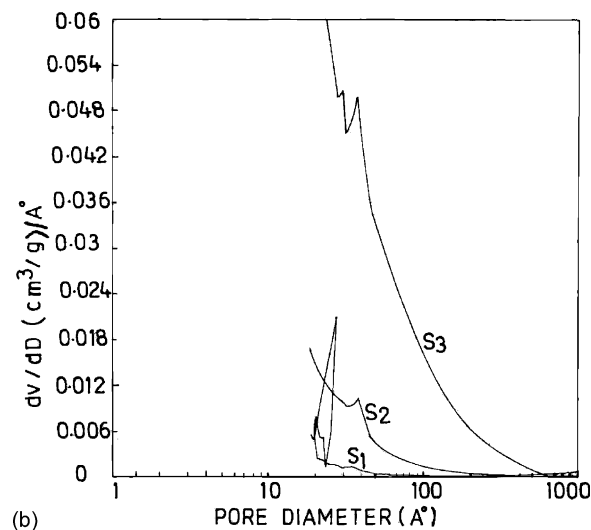


Fig. 2. DR plots of active carbon spheres from N₂ adsorption at 77 K.



(a)



(b)

Fig. 3. (a) Micropore size distribution (Horvath and Kawazoe) of ACS samples S₁, S₂ and S₃. (b) Mesopore size distribution (BJH) of ACS samples S₁, S₂ and S₃.

On the other hand, McEnaney [5] has proposed that pore diameter (d_M) is related to E_0 by the following equation:

$$d_M = \frac{\ln(41.26/E_0)}{0.56} \quad (3)$$

The surface properties obtained from adsorption studies applying DR and BET equations are given in Table 1. The average pore diameter obtained by applying the equation $d_{av} = 4V/S$ is also included in Table 1. Where V is the volume of nitrogen adsorbed in ml/g at relative pressure of 0.95 and S is the BET surface area in m²/g.

Some interesting observations can be made after the perusal of Table 1. The BET surface area varying from 201 to 2100 m²/g is a manifestation of progress of pore formation in micropore region. In all the three samples S₁, S₂ and S₃ the filling of micropores is indicated by a sharp rise in isotherms at very low relative pressure shown in Fig. 1. In

Table 1
Porous structure parameters of active carbon sphere samples

Sample	BET surface area (m ² /g)	DR V_{micro} (ml/g)	% Micropore volume	Adsorption energy, E_0 (kJ/mol)	Average pore diameter, d_{av} (nm)	Pore diameter, d_{D} (nm)	Pore diameter, d_{M} (nm)
S ₁	201	0.0944	80.00	15.72	2.00	1.52	1.72
S ₂	1150	0.5311	52.10	12.18	3.55	1.97	2.18
S ₃	2100	0.7379	35.32	10.29	3.90	2.33	2.48

Analysis temperature: 77 K; adsorbate used: N₂.

samples S₂ and S₃ ascending pattern after first point of inflection is due to cooperative mechanism of monolayer multilayer adsorption followed by capillary condensation. The total pore volume, along with micropore volume increases on increasing the duration of activation, but percentage of micropore volume in total pore volume decreases. This may be due to the widening of micropores as suggested earlier. The average micropore diameter d_{D} and d_{M} obtained by applying empirical Eqs. (2) and (3) suggested by Dubinin and McEnaney, respectively are in close agreement with each other and they are given in Table 1.

The pore size distribution curves of the samples S₁, S₂ and S₃ in micropore region obtained by N₂ adsorption at 77 K and analyzed by the Horvath and Kawazoe Method [19] are shown in Fig. 3a. As can be seen in this figure, peaks in the range 0.57–7.0 nm are present for the samples S₁, S₂ and 0.68–0.78 nm for the sample S₃. These are the pores, which in our opinion are responsible for the molecular sieving properties of the carbons studied. The mesopore size distribution curves of samples S₁, S₂ and S₃ obtained by the BJH method [20] are shown in Fig 3b. One can notice in this figure that there are peaks in the range 2.1–2.7, 3.3–4.0 and 2.8–4.0 nm for the samples S₁, S₂ and S₃, respectively. The progressive broadening of PSD from sample S₁ to S₃ is mainly due to pore widening attributed to activation conditions. The similar trend was shown by average pore diameters obtained from various equations given in Table 1.

3.2. Inverse gas chromatography at zero surface coverage

Gas chromatography, when used to characterize the stationary phase, is called inverse gas chromatography. In absence of specific interaction between alkanes, branched alkanes and ACSs, the retention time of appropriate probes (alkanes and branched alkanes) were measured on adsorbent materials. This essentially is adsorption measurement method carried out in dynamic condition. For small quantities of probes (retention time is independent of amount injected) Henry's law describes the adsorption. The specific retention volume of probes were calculated using the following equation [6]:

$$V_g = \left[\frac{t_i - t_0}{w} \right] F \left(\frac{273}{T} \right) \quad (4)$$

where V_g is the specific retention volume (ml/g), t_i the retention time of probe (min), t_0 the retention time of

methane (min), T the column temperature (K), w the mass of material packed in GC column (g) and F is the flow rate of carrier gas (ml/min) at ambient temperature (30 °C) and 1 atm pressure (1 atm = 101 325 Pa).

In the present work, from V_g measured at different temperatures the isosteric heat of adsorption (q^{st}) has been calculated by plotting natural logarithm of retention volume against reciprocal of absolute temperature using the following equation [6]:

$$q^{\text{st}} = R \left[\frac{d \ln V_g}{d(1/T)} \right] \quad (5)$$

In Fig. 4 representative plots of $\ln V_g$ versus $1/T$ for sample S₃ in respect of alkanes having carbon numbers 2–6 are shown. Plots are straight lines over wide range of temperatures. The numbers along side plots refer to the numbers of carbon atoms in n-alkanes. The upper vertical displacement of plots with carbon numbers indicates the enhancement in adsorptive potential reflected in increase in specific retention volume with chain length of probe. Similar linearity was observed for samples S₁ and S₂.

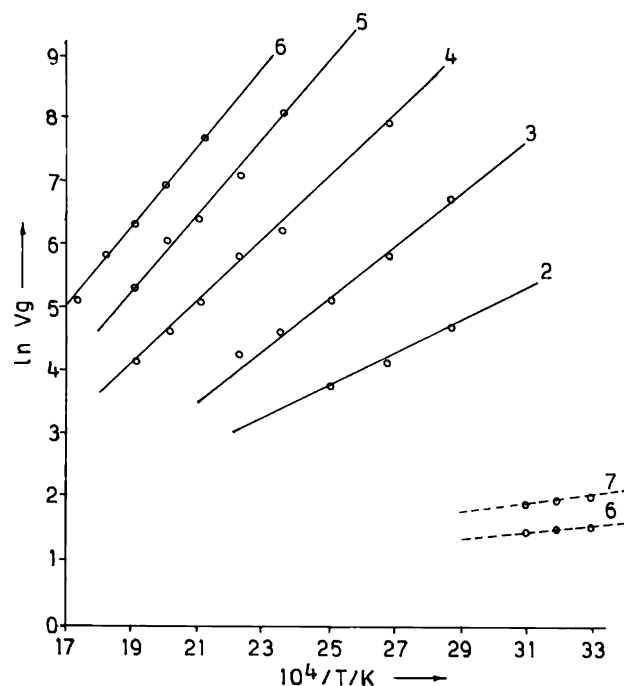


Fig. 4. Variation of specific retention volume with temperature for n-alkanes, S₃ (—), S₀ (---) (numbers of lines indicate numbers of carbon atoms).

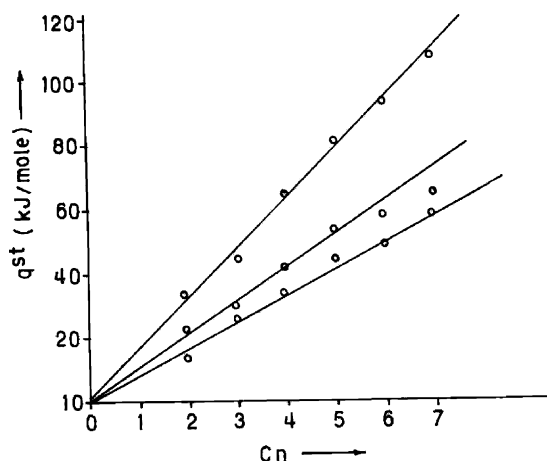


Fig. 5. Variation of q^{st} with n-alkane chain length.

The isosteric heat of adsorption (q^{st}) for each sample is plotted against number of carbon atoms (C_n) is shown in Fig. 5. The q^{st} values are highest for sample S_1 having smallest BET surface area, i.e. $201 \text{ m}^2/\text{g}$. This appears to represent the upper limit of adsorptive interaction of alkanes in narrow pores. The q^{st} values for n-heptane are given in Table 2.

The q^{st} values decrease sharply from sample S_1 to S_3 with increase in surface area. The increase in surface area for sample S_1 to S_3 should be associated with the enhancement of microporous nature of the sample. The sharp decrease in q^{st} values for sample S_3 should be probably due to reduction in ultramicroporosity (pore width $< 0.1 \text{ nm}$) and wide pore size distribution caused by pore widening. The pore widening is taking place mainly within the micropore region. It is also indicated from micropore volume obtained from DR-equation as shown in Table 1, which increases from sample S_1 to S_3 . In this region adsorption is followed by pore filling by cooperative effect is responsible in the enhancement of surface area. Nevertheless, the q^{st} values for sample S_3 are still 12 times higher to that of non-porous sample for n-heptane. The enhancement of potential energy in molecular size pores is more or less an established phenomenon. On the basis of theoretical calculations, it has been established that narrower the pore size higher the enhancement and maximum enhancement is observed in the pores having size in vicinity of twice the molecular diameter of the adsorbate.

In the present work, the difference in the free energies of adsorption of two subsequent n-alkanes and corresponding branched alkanes having same number of carbon atoms in

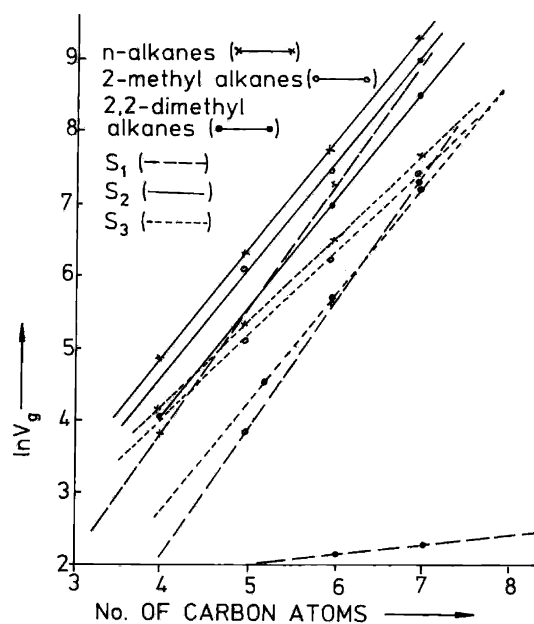


Fig. 6. Dependence of $\ln V_g$ of alkanes measured at 543 K on their numbers of carbon atoms.

the main chain and one or two methyl groups attached on second carbon atom of the chain were evaluated by IGC to understand the nature of interaction between adsorbate and adsorbent and additional information on molecular sieving property of active carbon spheres. It has been already reported that the free energy of adsorption of n-alkanes and corresponding branched alkanes is proportional to the number of carbon atoms in the main chain [9,21–23]. Logarithm of retention volume of each sample for n-alkanes and corresponding branched alkanes versus number of carbon atoms have been plotted and is shown in Fig. 6 which provides information about the pore structure of the carbons studied. Since free energy of adsorption ΔG is proportional to the logarithm of retention volume, the slope gives free energy of adsorption for a methylene group, i.e. ΔG_{CH_2} . The calculated free energy of adsorption ΔG_{CH_2} for all the samples shown in Table 3 are comparable to the free energies of adsorption for molecular sieving carbon [9,24]. However, the free energy of adsorption ΔG_{CH_2} systematically decreases from sample S_1 to S_3 probably due to pore widening in micropore region. As far as sample S_1 is concerned, it has already been shown earlier [7] that the enhancement in the adsorption potential in narrow pores gives rise to higher values of free energy of adsorption. The free energy of adsorption is highest for sample S_1 indicating the presence of very narrow pores. The IGC results are in tune with the surface properties shown in Table 1, such as sample S_1 is highly microporous having 80% micropore volume, average pore diameter 2.0 nm and micropore diameter 1.5 nm. Its average pore diameter is very close to micropore width obtained by Dubinin and McEnaney equation which shows narrow pore structure.

Table 2
Isosteric heat of adsorption of n-heptane on ACS samples

Sample	BET surface area (m^2/g)	q^{st} (n-heptane) (kJ/mol)
S_0	5	5.8
S_1	201	118.6
S_2	1150	86.6
S_3	2100	62.4

Carrier gas: N_2 ; flow rate: 30 ml/min; temperature: 543 K.

Table 3
Gas chromatographic results

Sample	BET surface area (m ² /g)	$-\Delta G_{\text{CH}_2}$ (kJ/mol)	$-\Delta G'_{\text{CH}_2}$ (kJ/mol)	$-\Delta G''_{\text{CH}_2}$ (kJ/mol)	$-\Delta'$ (kJ/mol)	$-\Delta''$ (kJ/mol)	$\gamma_{\text{s}}^{\text{d}}$ (mJ/m ²)
S ₁	201	7.75	7.90	0.90	7.22	19.53	323
S ₂	1150	6.77	6.70	6.77	1.24	3.49	247
S ₃	2100	5.34	5.19	6.77	0.90	4.29	153

Carrier gas: N₂; flow rate: 30 ml/min.

The molecular sieving behavior of the samples prepared has also been studied by using n-alkanes (NAs), 2-methylalkanes (MAs) and 2,2-dimethylalkanes (DMAs) as probe material. The critical sizes of these probes are evaluated by the sizes of molecules head are 0.36, 0.46 and 0.60 nm, respectively [15]. The difference in the free energies of adsorption of NAs, MAs and DMAs marked as ΔG_{CH_2} , $\Delta G'_{\text{CH}_2}$ and $\Delta G''_{\text{CH}_2}$ are presented in Table 3. The free energies of adsorption for sample S₁ increases marginally for NAs to MAs but decreases sharply for DMAs. This indicates that in the sample S₁ the pore size varies from 0.36 to 0.46 nm. Hence DMAs are completely excluded having very low value of free energy of adsorption, i.e. 0.90 kJ/mol. However, the free energies of adsorption for samples S₂ and S₃ are in general lower than confined to sample S₁ and differences of Δ values for normal and branched alkanes are not significant. This indicates the wide pore size distribution in sample S₂ and S₃, i.e. from 0.36 to 0.60 nm.

The surface excluded by MAs and DMAs is evaluated by measuring the average vertical shift of NAs to MAs (Δ') and NAs to DMAs (Δ'') on the carbon samples studied. The vertical shift for non-porous carbon (graphitized carbon black) [9] is deducted from vertical shift of carbon samples studied which indeed accounts for carbon atoms in the branched part of the molecule that cannot be accommodated in the same plane parallel to the surface. The Δ'' value shown in Table 3 is substantially higher for sample S₁ indicates the number of pores having diameter smaller than 0.6 nm are highest in Sample S₁ excludes DMA molecules almost completely. In case of sample S₂ and S₃ the Δ' and Δ'' values are smaller and in close agreement suggests that the majority of pores in these samples are accessible to MAs and DMAs. Low temperature adsorption gave the micropore range 0.57–0.7 nm for samples S₁, S₂ and 0.68–0.78 nm for Sample S₃ by pore size distribution. However, average micropore size was obtained around 1.5 nm on application of Dubinin and McEnaney equation. The micropore size and range obtained by molecular probe technique is smaller because this measured at elevated temperature, when the probe molecule can enter into smaller diameter pores. However, the pore size obtained from Dubinin and McEnaney equation is much higher because it is an average of whole micropore region includes pore upto 2.0 nm.

3.3. Dispersion component of surface energy

It is well known that the free energy of adsorption for n-alkanes varies linearly with their number of carbon atoms

independent of position of methyl groups in the chain. The difference in the free energy of adsorption of two n-alkanes having n and $n + 1$ carbon atom, ΔG_{CH_2} , is then independent of number of carbon atoms in the alkane probe, which makes this quantity a very useful parameter to represent the dispersive interaction capacity of solid surface. Dorris and Gray [22] proposed the method whereby ΔG_{CH_2} is used to evaluate the dispersive component of the surface energy, $\gamma_{\text{d}}^{\text{s}}$, by the formula:

$$\gamma_{\text{d}}^{\text{s}} = \frac{(\Delta G_{\text{CH}_2})^2}{4\gamma_{\text{CH}_2}(Na)^2} \quad (6)$$

where ΔG_{CH_2} is the free energy of adsorption for a $-\text{CH}_2-$ group and is obtained from slope of $\ln V_{\text{g}}$ versus the number of carbon atoms of a series of n-alkanes, γ_{CH_2} the surface energy of a surface made of $-\text{CH}_2-$ groups only and equal to 35.6 mJ/m² at 293 K [25], a the area of a $-\text{CH}_2-$ group (0.06 nm²) and N is Avogadro's number. Hence, all the parameters of above equation are known except $\gamma_{\text{d}}^{\text{s}}$ which can be calculated.

The surface energy data obtained using Eq. (6) above is given in Table 3, which further confirms the narrowest pore structure present in the sample S₁. The free energy of adsorption is maximum for sample S₁ having average micro pore size ~ 1.5 nm. The dispersive component of the surface energy $\gamma_{\text{d}}^{\text{s}}$ expresses the potential of a solid to undergo non-specific interaction. Since IGC experiments were carried out at zero surface coverage, the $\gamma_{\text{d}}^{\text{s}}$ values correspond to most active sites. The percent microporosity obtained by DR equation using N₂ gas adsorption

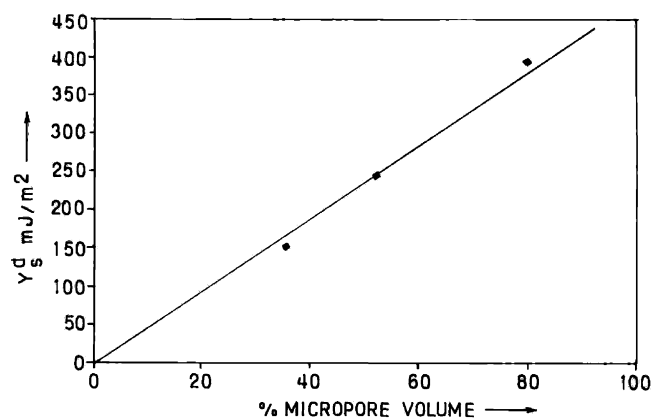


Fig. 7. Variation of dispersive component of surface energy with % micropore volume.

measurements at 77 K, have linear relationship with γ_d^s as shown in Fig. 7 because micropores corresponds to most active sites due to overlapping of surface potential in narrow pores. Further, γ_d^s is also correlates well with active surface area [26]. However, concept of surface area is superfluous in case of microporous solids due to micropore filling at low relative pressure, nevertheless surface area values do indicate adsorption capacity of the solid.

4. Conclusions

In the present work, the porous samples of active carbon spheres were characterized using adsorption studies at liquid nitrogen temperature and IGC analysis at elevated temperature. The pore size and range evaluated by IGC technique is smaller than obtained by PSD of N₂ adsorption data. The variation is probably due to difference in analysis conditions mainly temperature. Another aspect to this difference may be due to the fact that in IGC measurements only tiny amount of alkanes are injected in the GC column containing ACSs samples, amounts which are insufficient to cover the surface with monolayer of adsorbed alkane probes. The surface explored by few injected probe molecules (corresponding to the very initial part of the isotherm) will not be representative of the total surface of the solid. Hence, IGC at zero surface coverage principally address the most active sites, which retain the probe molecules most strongly, in this instance the micropores whereas BET analysis includes all types of pore range. Hence, IGC and BET results differ.

The heat of adsorption, free energy of adsorption and dispersive component of surface energy measured by IGC is highest for microporous sample S₁ with narrow pore structure and narrow pore size distribution. This is further confirmed by the adsorption data analysis. It can be concluded that molecular sieving properties are strongly dependent on temperature at which these are used apart from the inherent pore structure and pore size distribution available in the adsorbent.

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