Studies in Mixed Adsorbent Systems : Adsorption of Water Vapours on Carbogels

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The water adsorption isotherms determined at 35°C on different carbogels prepared by the precipitation of silica gel from a solution of sodium silicate containing suspensions of carbon black, original sugar charcoal and 1000°C degassed sugar charcoal indicate that the two adsorbents form intimate mixtures by the precipitation of particles of silica gel in a fine state of subdivision within the wider capillary channels. This is further supported by pore size distribution curves. The maximum amounts of different carbons required for producing optimum effect are found to be 16, 41 and 13% respectively in the case of carbon black, original sugar charcoal and 1000° C-degassed sugar charcoal.

I T appears from a perusal of the literature[1-6] that several types of adsorbents, both mixed and pure, have been used from time to time and a continuous search is being made for developing newer adsorbents and improving upon the older ones. The present paper describes the adsorption of water vapour on carbogels prepared from silica, carbon black and charcoal.

Materials and Methods

Original sugar charcoal[7], 1000°C-degassed sugar charcoal[8], carbon black, freshly precipitated silica gel, and their several admixtures were used as adsorbents. Redistilled water was used as adsorbate.

Preparation of carbogels — A known fixed volume of sodium silicate solution ($d = 1.08$ g/cc) was mixed with varying amounts (10g to 40g) of carbon and the suspensions stirred vigorously for 1 hr. A solution of $1N$ hydrochloric acid was then added to the suspension dropwise, with stirring, till the mixture became slightly acidic. It was further stirred vigorously for 1 hr and more acid added, if necessary. The excess of acid was removed by repeated washing with distilled water. Several mixtures containing different proportions of charcoal and silica gel were prepared in this way. The composition of various samples of carbogels obtained from three different carbon samples are given in Table 1.

Water vapour adsorption — The water vapour adsorption was determined at 35°C gravimetrically using a modified Mc Bain quartz spring balance[9].

Results and Discussion

The three carbon samples, i.e., carbon black, original sugar charcoal and 1000°C-degassed sugar charcoal, were selected keeping in view their different surface behaviour and surface characteristics. The carbon black sample has a low surface area and

is essentially non-porous and has only traces of combined oxygen and hydrogen. The two samples of sugar charcoal are highly porous and have almost same surface area. But they differ in oxygen content. The original sugar charcoal is associated with 30% of combined oxygen whereas the degassed sample is almost free of combined oxygen.

Carbon black-silica system — The adsorption isotherms of water on carbon black, silica gel and their mixtures (Samples I, II and III, Table 1) at 35°C are shown in Fig. 1. It is seen that the adsorption of water vapour on silica gel is much larger as compared to that on carbon black at all relative vapour pressures. This can be attributed to different surface characteristics and pore structures of silica gel and carbon black.

Silica gel is highly polar and has terminal hydroxyl groups which interact with OH group of water and could bind them by hydrogen bonding as shown in structure (I)

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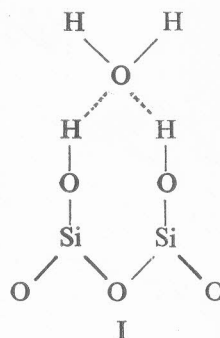
Several workers[10-12] have shown that the amount of water adsorbed in silica gel is directly related to the number of hydroxyl groups present on its surface. Furthermore, silica gel is porous and water can condense by capillary condensation at higher relative vapour pressures.

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TABLE 1 — PERCENTAGE COMPOSITION OF VARIOUS ADSORBENT SAMPLES

Absorbent	$SiO_2(\%)$	$C(\%)$
Charcoal	0.0	100.0
Carbogel I	89.9	10.1
Carbogel II	83.7	16.3
Carbogel III	73.1	26.9
Carbogel IV	59.2	40.8
Carbogel V	47.0	53.0
Carbogel VI	29.2	70.8
Carbogel VII	87.7	12.3
Carbogel VIII	74.1	25.9
Silica gel	100.0	0.0

Carbon black is essentially non-porous and has little oxygen on its surface and therefore the chances of interaction with water molecules are less.

In the case of carbogel samples, the water up take initially increases with increase in carbon black content from 10% to 16% and thereafter it decreases. The adsorption isotherm for carbogel I which contains 90% silica and 10% carbon lies in between those of pure silica gel and carbon black. However the water uptake by carbogel II which contains 87.3% silica and 16.7% carbon black is much more than even pure silica gel at all relative vapour pressures. It is clear from Fig. 1 that the amount of water adsorbed by carbogel II is about one and a half times compared to that of pure silica gel at saturation vapour pressure.

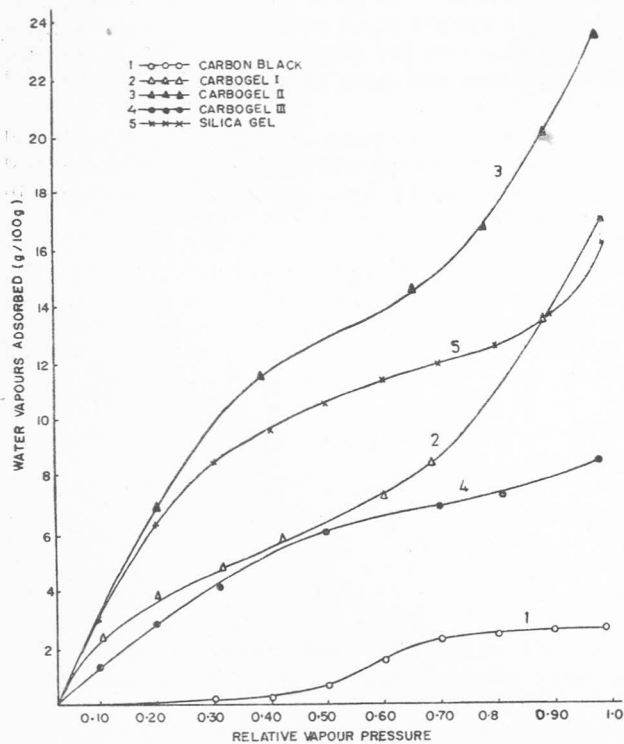This increase in the amount of water vapour adsorbed cannot be attributed to any increase in the interaction between the water molecules and the carbogel surface since the presence of carbon black could result only in a decreased interaction. The carbon black is likely to block some of the active sites which could be taken up by the water molecules on the surface of silica gel as has been observed with carbogel I. This increase, therefore, appears to be due to the precipitation of particles of carbon black in a fine state of subdivision within the wider capillary pores of silica gel, thus giving rise to a larger number of extremely small capillary channels. The width of these channels may exceed only a few molecular diameters, thus causing the potential field from opposite walls to overlap so that the attractive force acting on the adsorbate molecule increases. There is consequently an increase in adsorption.

The adsorption isotherm of carbogel III containing 73% of silica and 27% carbon black is lower than that of carbogel II and lies in between that of pure constituents. The adsorption isotherm lies even lower than that of carbogel I. It appears that when the carbon content of mixture is about 16%, the packing of particles of carbon black into the interstices of silica gel is maximum. When the amount of carbon black increases to more than 16%, the extra amount of carbon black will not be present in the form of an intimate mixture, but will lie as such and can even block some of the fine capillaries produced already. Thus the amount of water vapour adsorbed decreases.

That the carbogels formed are intimate mixtures of the two adsorbents with the two constituents present in the interstices of each other and not a simple mixture of the two is shown in Fig. 2, where experimental adsorption isotherms for various samples are compared with calculated adsorption isotherms. The adsorption isotherms for pure constituents are also reproduced from Fig. 1 for comparison purposes. The calculated absorption isotherms are obtained as follows :

Carbogel II contains 83.7% of silica and 16.3% carbon black, i. e. 1g of carbogel will contain 837 mg of silica gel and 163 mg of carbon black. The adsorption of water vapour at different relative vapour pressures on 837 mg of silica gel and 163 mg of carbon black has been calculated from their respective isotherms obtained experimentally. The sum of two adsorption values at different relative vapour pressures when plotted gives the calculated adsorption isotherm for the carbogel.

As expected the calculated adsorption isotherms lie in between the adsorption isotherm of silica gel and carbon black. The experimental adsorption isotherm lies much higher for carbogel II and lower for carbogels I and III as compared to their calculated adsorption isotherm. This clearly shows that the two constituents of the carbogel do not lie side by side but they form an intimate mixture. Another evidence for the presence of intimate mixture of the two constituents is provided by the pore size distribution curves (Fig. 3) of pure constituents and the various carbogels. The pore size distribution curves have been calculated applying Kelvin equation. Carbogel II has a much larger proportion of capillary

Fig. 1 — Water vapour adsorption isotherms on silica gel, carbon black and their admixtures at 35°C.
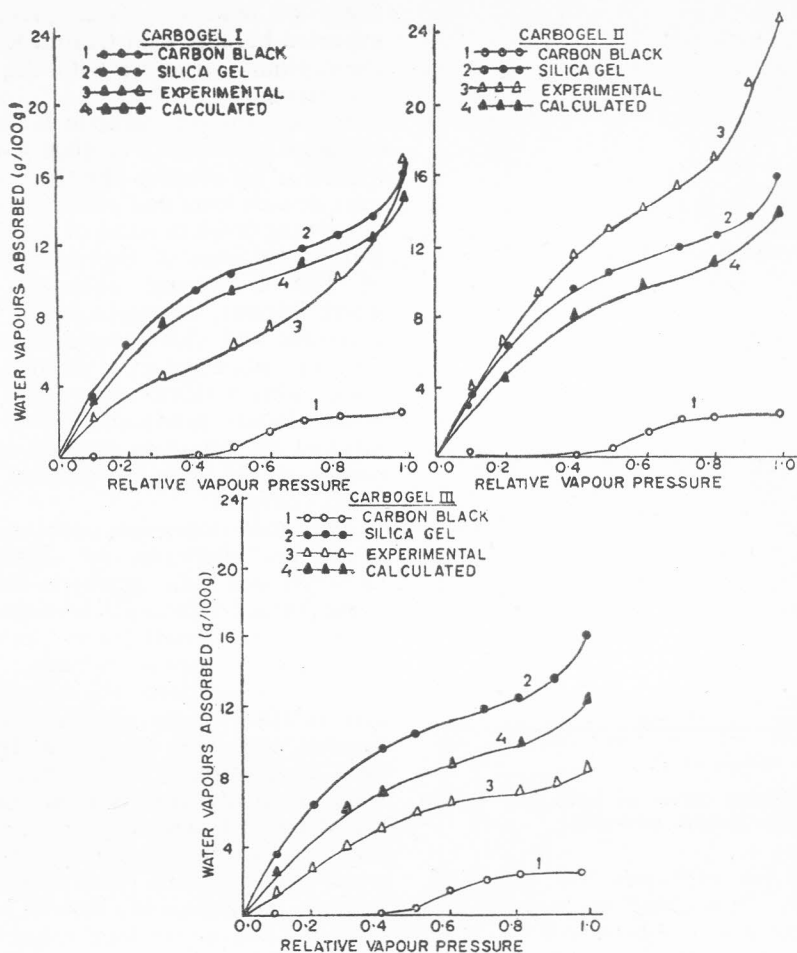
Fig. 2—Experimental and calculated adsorption isotherms of water vapour on various carbogel samples at 35°C.

channels than the pure constituents while carbogels I and III have much smaller number of capillary channels. This indicate that the quantity of carbon needed to produce optimum effect is equal to 16.3% and an amount less or higher than this does not produce an intimate mixture leaving some carbon as such and this may completely block some of the fine capillary pores already produced.

Original sugar charcoal-silica system — Both silica gel and charcoal adsorb appreciable amounts of water vapour although the adsorption is more in case of silica gel at lower relative vapour pressures indicating that it has more micro-capillary pores compared to charcoal (Fig. 4). The adsorption of water vapour at higher relative vapour pressures, i.e., above 0.75 relative vapour pressure it is slightly more in the case of charcoal compared to silica gel but the amount adsorbed at saturation vapour pressure is almost the same. The adsorption isotherms for carbogels IV and V which contain 41 and 53% carbon respectively, are higher than those for pure constituents after relative vapour pressure of 0.25 indicating that the fixation of charcoal in the interstices of silica gel and precipitation of silica gel in the wider capillary pores of charcoal result in narrowing down

of capillary pores leading to increase in the adsorption.

A comparison of the isotherms for carbogels IV and V shows that the adsorption of water vapour on carbogel V is slightly more compared to that on carbogel IV at lower relative vapour pressures and is slightly less at higher relative vapour pressures. The two isotherms cross each other at relative vapour pressure of about 0.45. Since adsorption at lower relative vapour pressures (i.e. $\leqslant$ 0.6) is predominant in smaller capillary pores (micropores) it is evident that there is an increase in the number of smaller pores as a result of the fixation of additional amount of carbon. The decrease in the adsorption of water vapour at higher relative vapour pressures is due to conversion of some of the wider capillary pores into smaller capillary pores.

In the case of carbogel VI, which contains about 70% carbon, the adsorption of water vapour is much less as compared to carbogels IV and V and is even less as compared to pure silica gel upto relative vapour pressures of 0.6. This indicates that the additional amount of carbon has gone into the micro-capillary pores blocking some of them.

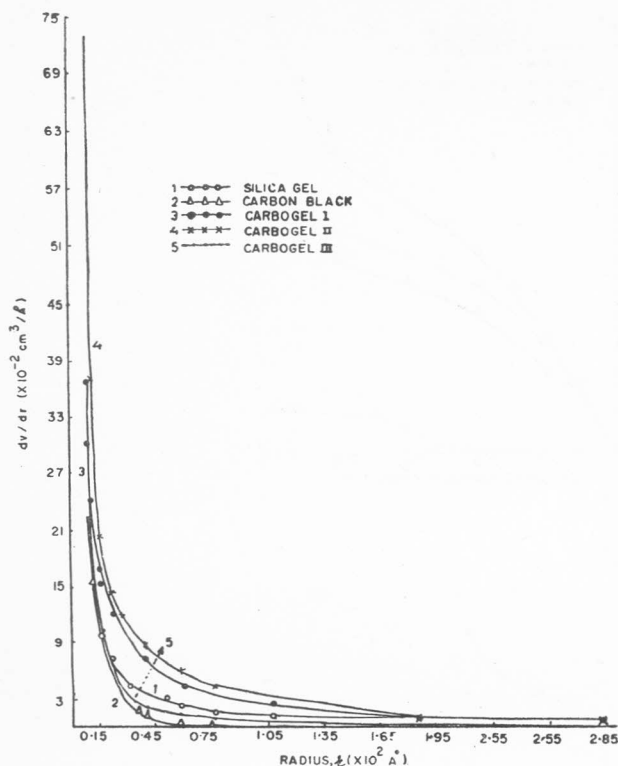*1000°C-Degassed charcoal-silica gel* — The water

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Fig. 3 — Pore size distribution curves of silica gel, carbon black and various carbogels.

adsorption isotherms for carbogels VII and VIII, are shown in Fig. 5. The shape of isotherm for 1000°C-degassed charcoal is of V type of BET classification, indicating that capillary condensation has taken place in wider capillary pores in the middle range of relative vapour pressures. This is to be expected because heat treatment at 1000°C breaks-up the capillary structure with the formation of wider capillaries.

The adsorption isotherm for carbogel VII, which contains about 13% of 1000°C-degassed charcoal is higher at all relative vapour pressures compared to pure constituents and carbogel VIII. This indicates narrowing down of some of the wider capillary pores. But in the case of carbogel VIII containing 26% of 1000°C-degassed charcoal the adsorption of water vapour is decreased at all relative vapour pressures and also crosses the adsorption isotherm for pure silica gel at a relative vapour pressure of 0.45. This indicates that some of the fine capillary pores already produced in the carbogel have been blocked by this extra amount of charcoal as stated earlier in the case of carbon black and original sugar charcoal.

Adsorption-desorption isotherms — The adsorption-desorption isotherms on original sugar charcoal, silica gel and their carbogels reveal following significant features: Silica gel does not show any hysteresis whereas for charcoal the hysteresis persists even upto zero relative vapour pressure, i.e. the desorption curve does not meet the adsorption curve even at zero relative vapour pressure showing that a certain amount equivalent to approx. 2g/100g of water has been chemisorbed. To ensure if this amount of water is really chemisorbed, the temperature is raised by 10°C and the system evacuated for a long time. It is found that not even a small amount of water gets desorbed. This means that this water is held on the surface of charcoal by chemical or quasi-chemical forces. In fact, it has been shown by Puri *et al.*[13], that original sugar charcoal which contains chemisorbed oxygen, disposed off as CO_2 on high
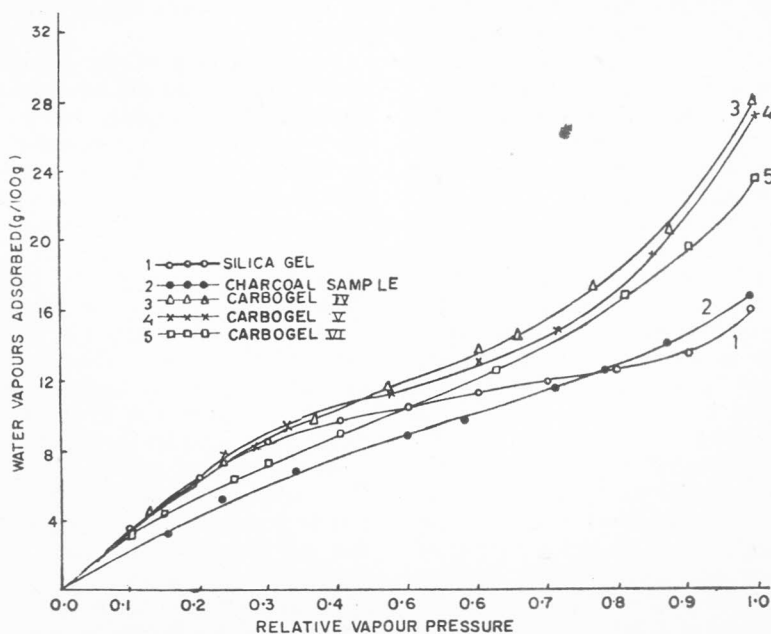

Fig. 4 — Adsorption isotherms of water vapour on silica gel, original charcoal and their admixtures at 35°C.
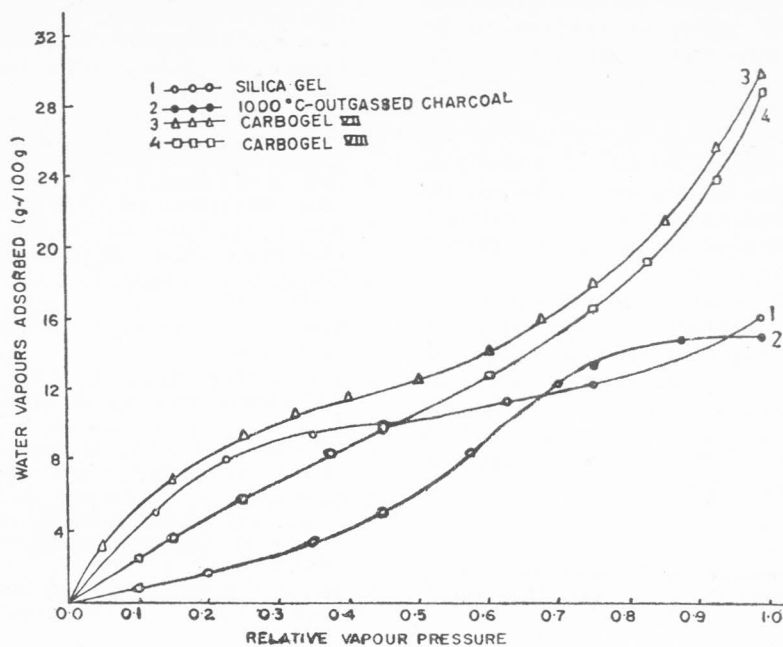
Fig. 5 — Adsorption isotherms of water vapour on silica gel, 1000°C-degassed charcoal and their admixtures at 35°C.

temperature evacuation, binds a certain amount of water which amounts to about 1 mol of water per mol of oxygen present on the surface.

In the case of carbogel samples, all isotherms show hysteresis and the desorption branch meets the adsorption branch at a relative vapour pressure between 0.4 and 0.5. The hysteresis loop tends to narrow down as the percentage of silica gel goes on increasing. In other words the area of hysteresis loop is dependent upon the pore size available in a particular sample. But the mutual packing of particles of one adsorbent into the interstices of the other results in a decrease in the pore size. It appears that the area of hysteresis loop is also an inverse function of pore size present in an adsorbent.

Furthermore the point of inception of hysteresis is almost the same in all the samples of carbogel. Earlier workers[14,15] have found that the point of inception of hysteresis should correspond to pores having radius equal to or larger than four times the radius of adsorbate. This means that hysteresis cannot occur in capillaries having radius less than four molecular radius of the adsorbate. This is in agreement with the results presented in this paper. The desorption curve meets the adsorption curve at a relative vapour pressure close to 0.40 which corresponds to capillaries having radius 10.6Å which is slightly larger than four times the radius of water adsorbate taking its radius to be 1.7Å.

The adsorption-desorption isotherms of water vapour for 1000°C-degassed charcoal, silica gel and their carbogels show that the desorption branch meets the adsorption branch at a relative vapour pressure between 0.4 and 0.5 in all carbogel samples, in agreement with the observations made earlier in the case of original sugar charcoal. The area of hysteresis loop also increases with decrease in the

TABLE 2 — SPECIFIC SURFACE AREAS AND NET HEATS OF ADSORPTION OF WATER VAPOUR ON VARIOUS ADSORBENTS

Adsorbent	Surface area (m²/g)		Net heat of adsorption (cal/g mol) E_1-E_L
	BET	Herkin's-Jaura	
Silica gel	68	65	540.0
Original sugar charcoal	89	100	358.0
1000°-Degassed charcoal	—	—	620.0
Carbon black	48	43	902.0
Carbogel I	59	65	184.0
Carbogel II	98	112	438.0
Carbogel III	84	92	301.0
Carbogel IV	109	94	325.0
Carbogel V	99	93	434.0
Carbogel VI	87	91	440.0
Carbogel VII	—	—	441.0
Carbogel VIII	—	—	263.0

amount of silica gel in the sample. This again confirms that the fine particles of silica gel have penetrated in the wider capillary pores of charcoal and that the charcoal granules have found a place within the wider capillaries of silica gel.

Surface area — The surface area of the carbogels have been calculated using the standard BET and Herkin-Jaura's method using water adsorption isotherms. The values of $E_1—E_1$, calculated from BET equation, which gives the net heat of adsorption are given in Table 2. It is clear from Table 2 that the net heat of adsorption lies within the range of physical adsorption indicating that the adsorption of water is physical. The surface areas of various samples have been included in Table 2. They have been calculated assuming the area covered by a water molecule to be 10.8 Å². The surface areas calculated

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by two methods are comparable but the surface area of carbogel II is quite higher as compared to the surface areas of pure constituents indicating that the two adsorbents have formed an intimate mixture giving rise to an increase in surface area.

It appears from the results presented above that the nature of carbon surface, particle size and pore size distribution of the carbon used influence the water vapour adsorption properties of the carbogel. It is worthwhile noting that the amount of carbon required to produce optimum effect in the case of original sugar charcoal—silica gel system is considerably higher (40%) as compared to that (16%) required in the case of carbon black-silica system or 1000°C-degassed charcoal-silica system. This may be due to the fact large sized particles of original charcoal may prevent its entry into the fine capillary pores of silica gel, until the amount of carbon in the sample is extremely high.

References

1. LEBODA, R., WAKSMUNDZKI, A., SUPRYNOWICZ, Z. & WAKSMUNDZKA-HAJNOS, M., Chem. Anal. (Warsaw), 21 (1976), 165.

2. BEBRIS, N. K., VOROBEVA, R. G., KISELEV, A. V., NIKITIN, YU. S., TARASOVA, L. V., FROLOV, I. I. & YASHIN, YA. I., J. Chromatogr., 117 (1976), 257.

3. TANAKA, H., TANAKA, T. & TANAKA, T., Chem. Abstr., 85 (1976), 197520d.

4. TSITSISHVILI, G. V., Zh. Fiz. Khim., 46 (1972), 3016.

5. MORIMOTO, T., NAGAO, M. & IMAI, J., Bull. chem. Soc. Japan, 47 (1974), 2994.

6. PURI, B. R., PARKASH, S. & SINGH, D. D., J. scient. ind. Res., 21D (1962), 158.

7. PURI, B. R., SINGH, D. D., NATH, J. & SHARMA, L. R., Ind. Engng Chem., 50 (1958), 1071.

8. BANSAL, R. C., DHAMI, T. L. & PARKASH, S., Carbon, 15 (1977), 157.

9. BANSAL, R. C., DHAMI, T. L. & PARKASH, S., Carbon, 16 (1978), 389.

10. BASSETT, D. R., BOUCHER, E. A. & ZETTLEMOYER, A. C., J. colloid interface Sci., 27 (1968), 649.

11. BOER, J. H. DE, HERMANS, M. E. A. & VLEESKENS, J. M., Koninkl. Ned. Akad. Wetenschap. Proc. Ser., B., 60 (1957), 43-53, 54-9; Chem. Abstr., 51 (1957), 11806l.

12. BELYAKOVA, L. D., DZHIGT, O. M. & KISELEV, A. V., Zhur. Fiz. Khim., 31 (1957), 1577.

13. PURI, B. R., MURARI, K. & SINGH, D. D., J. phys. Chem., 65 (1952), 37.

14. HIGUTI, I. & IWAGANI, Y., J. phys. Chem., 56 (1952), 921.

15. COHN, L. H., J. Am. chem. Soc., 60 (1938), 433.