Thermochimica Acta, 55 (1982) 253–267
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

STRUCTURAL AND SURFACE CHARACTERISTICS OF PURE AND LOW MOLECULAR WEIGHT OLIGOMER-CONTAINING SILICA GELS

T.M.EL-AKKAD

Chemistry Department, Faculty of Science, Ain Shams University, Abbassia, Cairo (Egypt)

(Received 15 September 1981)

ABSTRACT

The molecular weight of water soluble oligomers which can be included in inorganic gels during their precipitation affects greatly the surface and structural properties of these gels. The structural and phase changes of the pure and polyglycol 400 containing silica gels were studied by X-ray and differential thermal analysis. The intensity of the broad band, which may be correlated with the start of conversion from β to α quartz, decreased by inclusion of polyglycol 400 in silica gel. The inclusion led to retardation of the dehydroxylation of the gel. On thermal treatment marked variations in the surface area and pore volume were also observed.

The effect of the replacement of hydroxyl groups from the surface of the pure and 10% polyglycol containing silica gels thermally treated at 110°C with different acid centers, namely F^-, I^-, SO_4^{2-} and PO_4^{3-} ions, was discussed. The pure gel exhibited a higher ability to exchange with the previous ion centers than the 10% polyglycol containing silica gel. On the other hand, the latter has a higher tendency than the former for the rehydration process. In general, marked variation in nitrogen uptake whether in the mono or multilayer regions was observed due to the replacement of OH groups with different acid centers.

INTRODUCTION

Inclusion of organic polymers, either natural or synthetic, in inorganic gels has proved to have a significant bearing on their porosity character, and the high-pressure mercury technique adopted by Basmadjian et al. [1] to follow changes in pore volume distribution can only be applied for large-size pores. In previous studies, the bearing of the inclusion of water soluble polymers on the surface and textural characteristics of a number of oxide gels, namely, alumina [2,3], titania [4], vanadia [5], and zirconia [6] was studied.

In the preparation of silica gel, two groups of factors or conditions are identified as responsible for the development of the texture of the xerogel [7–11]. They are either conditions which promote the growth of globules or conditions which lead to stabilization of the hydrogel particles that include amongst other factors the substitution of the intermicellar water by an organic liquid.

In the present investigation, precipitation of the silica gel is affected by the inclusion in its matrix of a low molecular weight oligomer. The bearing of the inclusion of polyglycol, with a molecular weight of 400, on the structural, surface and porosity characteristics of the silica gel presents an interesting study.

MATERIAL AND TECHNIQUE

Polyglycol-400 was kindly supplied from the Hoechst Company, West Germany. Its inclusion in the precipitated silica gel was carried out by dissolving it in a 5% solution of sodium silicate (BDH grade) and the gel was then precipitated by the addition of concentrated ammonia, filtered and dried at room temperature over P_2O_5 to constant weight. Two such gel preparations were obtained by the inclusion of 2.5% and 10% by weight of polyglycol-400, in addition to a reference of pure silica gel.

Dehydration of precipitated gels at temperatures between 110 and 550°C was carried out in vacuo for 5 h by heating the tested sample in situ at a rate of 2.5–3°C min^{-1} using a small electric tubular furnace.

X-Ray diffraction patterns were obtained by means of a GEXRD-6 unit using Cu Kα-radiation. Observed d-values and intensities, I, were compared with reference data in the JCPDS files [12].

Differential thermal analysis (DTA) was carried out using a Heraeus thermo-analyzer 500 S.

Adsorption–desorption isotherms of nitrogen at −195°C were determined using a conventional volumetric apparatus [13].

RESULTS AND DISCUSSION

X-Ray diffraction patterns

XRD patterns for pure and the two polyglycol-containing silica gels thermally treated at 550°C, shown in Fig. 1, indicate clearly a decrease in the intensity displayed in the pure gel pattern with the increase in polyglycol content, an effect that may be correlated with the start of conversion from the β to the α-form of quartz [14].

Differential thermal analysis

DTA curves shown in Fig. 2 for pure, 2.5% and 10% polyglycol 400-containing silica gels reveal a low temperature endothermic peak at 150°C

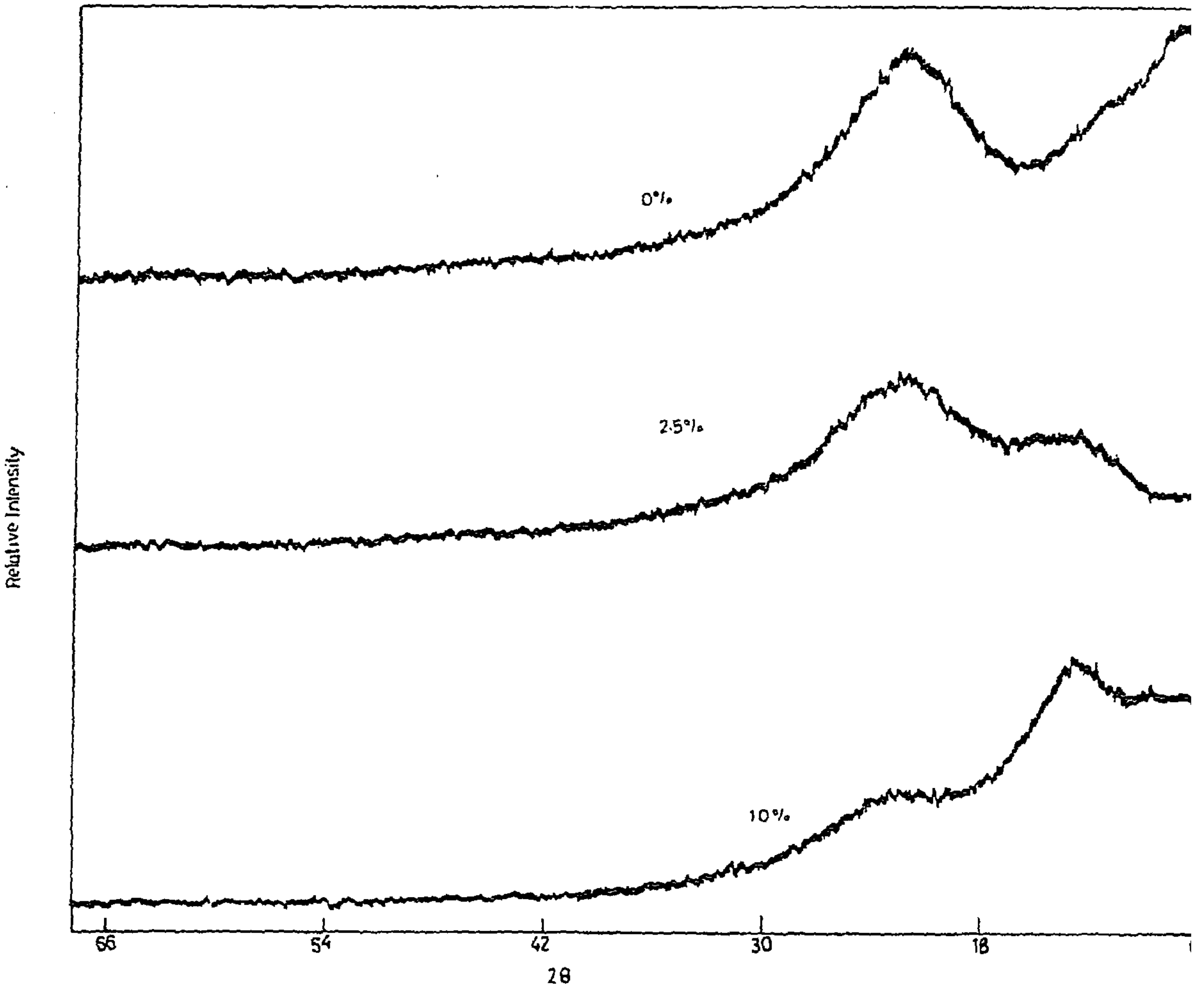


Fig. 1. X-Ray analysis of pure silica gel and silica gel containing polyglycol 400.

correlated with the dehydration of the gel, and an exothermic peak at 575°C that may be correlated with the phase change from the β- to the α-form of quartz [14].

Nitrogen isotherms

Adsorption–desorption isotherms of nitrogen at −195°C on pure, 2.5% and 10% polyglycol 400-containing silica gels thermally treated at 110–550°C are shown in Figs. 3–7. The isotherms are type II of Braunauer's classification [15] and invariably display (i) a high pressure hysteresis loop, indicative of a mesoporosity character that is maintained over the whole range of thermal treatment, (ii) a well-defined or even sharp knee at low P/P^0 values, indicative of a microporosity character. Thus the tested samples are invariably of a mixed porosity character.

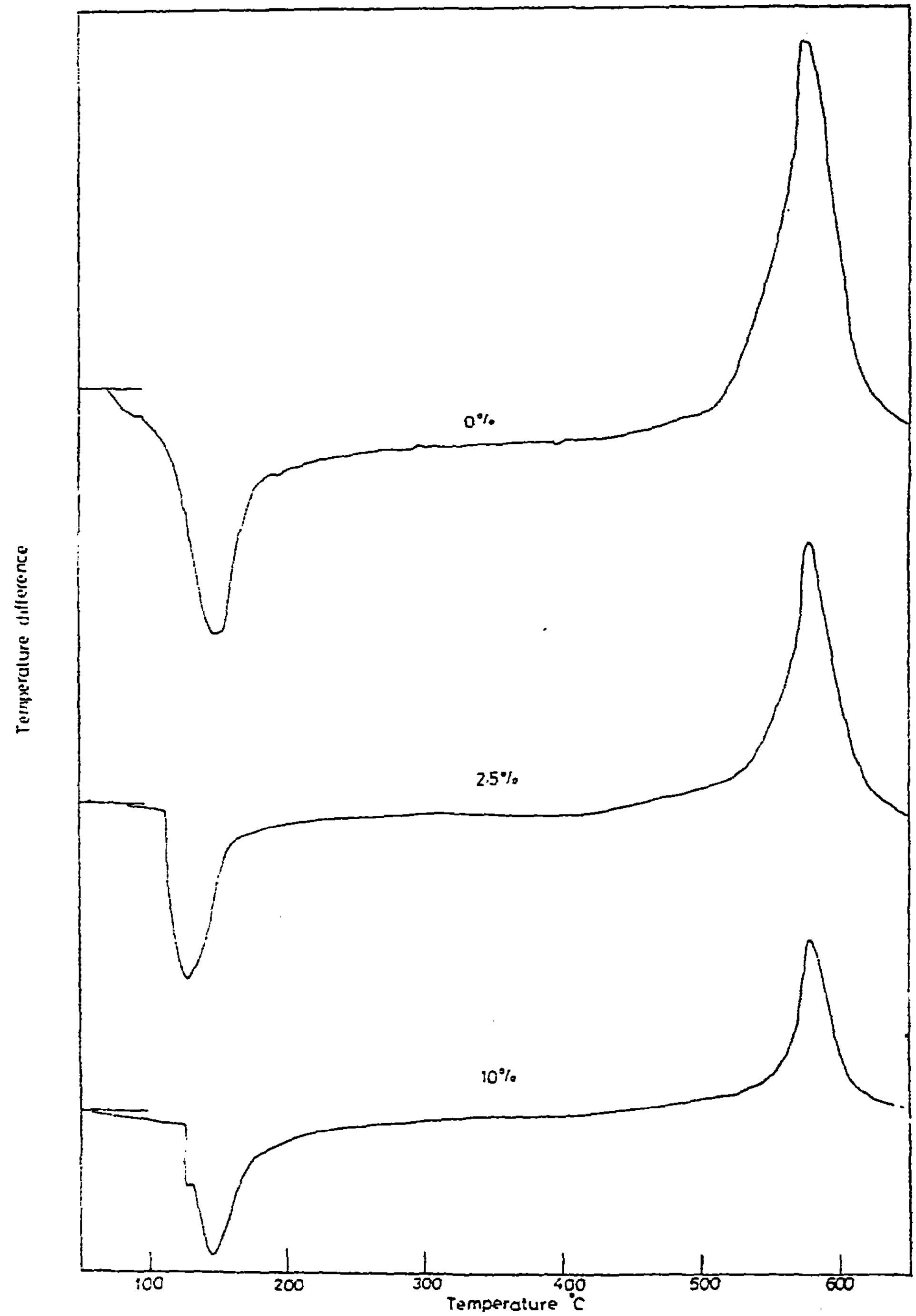
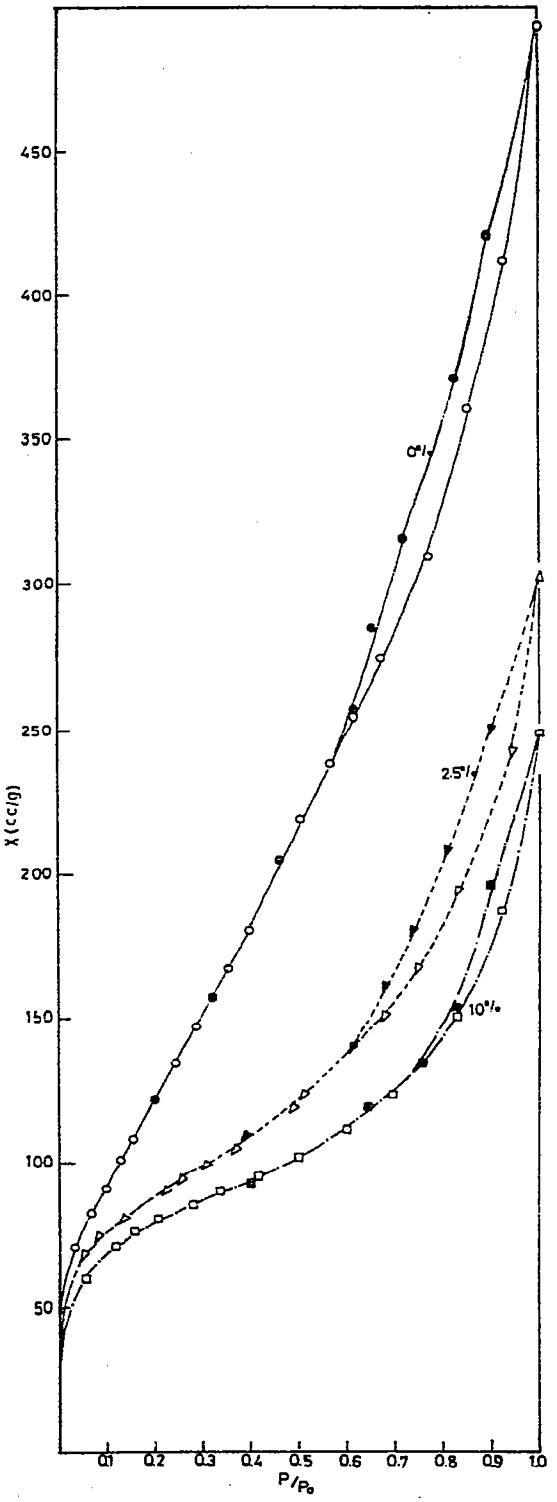


Fig. 2. DTA curves for pure silica gel and silica gel containing polyglycol 400.

From analysis of the adsorption isotherms by the BET equation [16], the specific surface area values $S_{\mathrm{BET}}^{\mathrm{N_2}}$ ($\mathrm{m^2\ g^{-1}}$) were computed, adopting a cross-sectional area for the nitrogen molecule of 16.2 Å^2 [17] (cf. Table 1); the values are in fair agreement with the S_t-values. The pore-size distribution



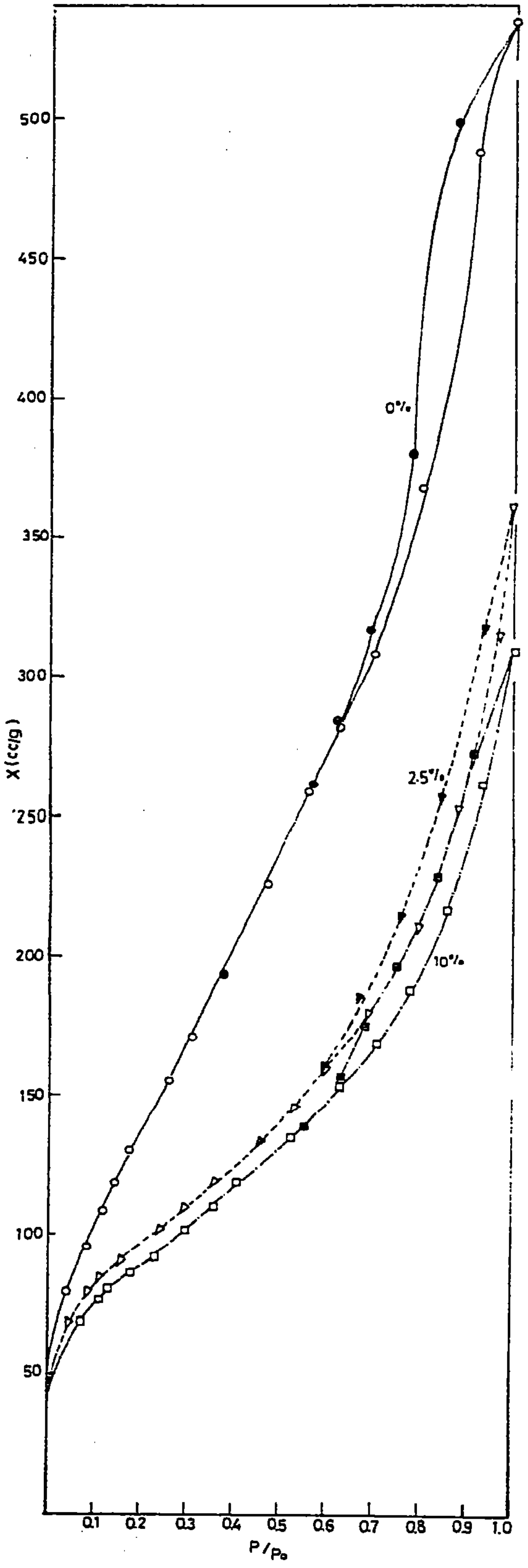
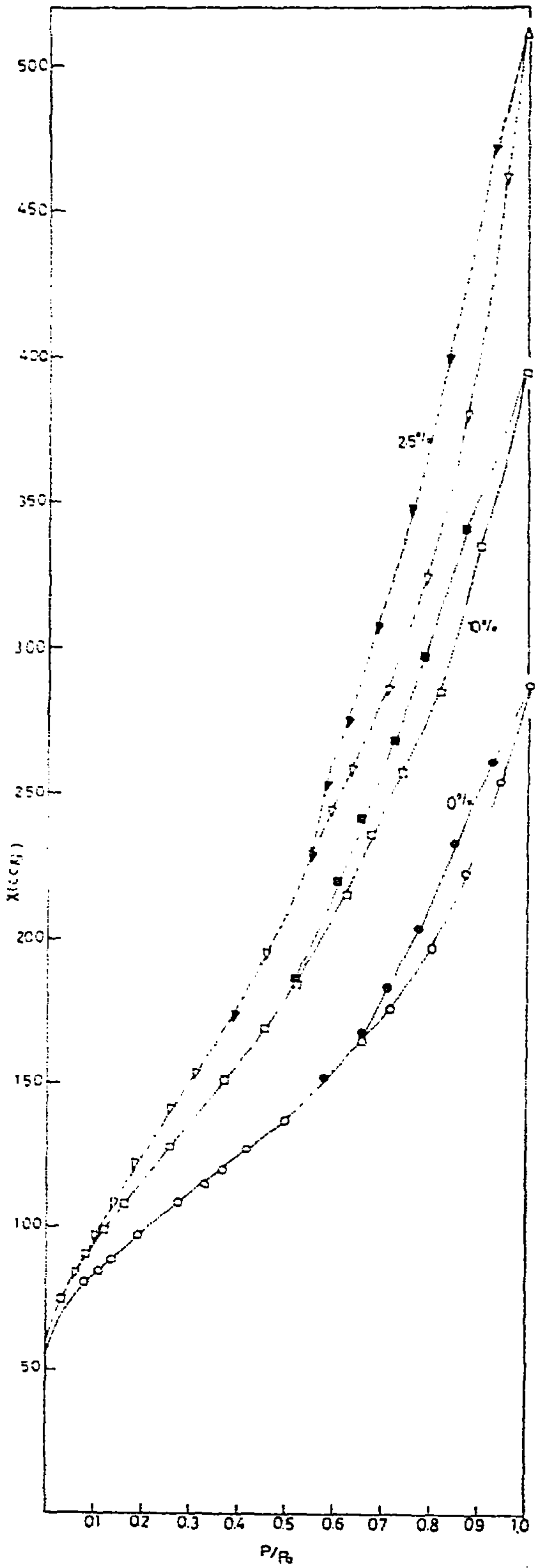


Fig. 3. Adsorption–desorption isotherms of nitrogen on pure silica gel and silica gel containing polyglycol 400 heated at 110°C.

Fig. 4. Adsorption–desorption isotherms of nitrogen on pure silica gel and silica gel containing polyglycol 400 heated at 200°C.



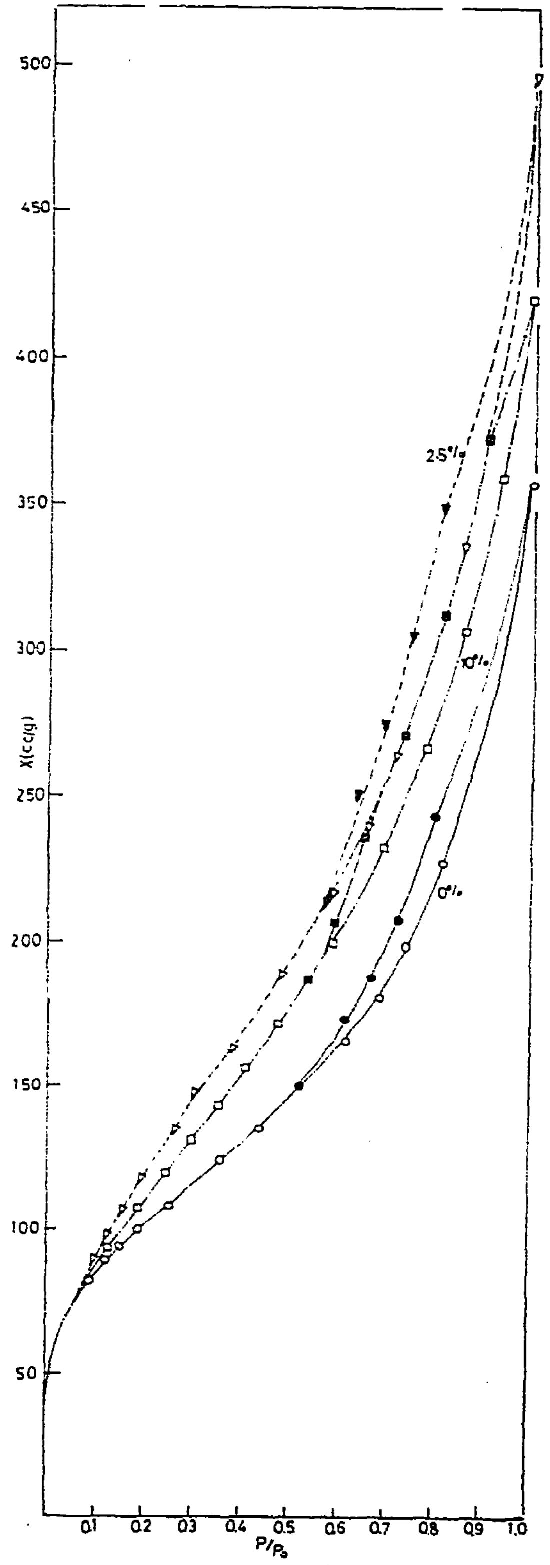


Fig. 5. Adsorption–desorption isotherms of nitrogen on pure silica gel and silica gel containing polyglycol 400 heated at 300°C.

Fig. 6. Adsorption–desorption isotherms of nitrogen on pure silica gel and silica gel containing polyglycol 400 heated at 400°C.

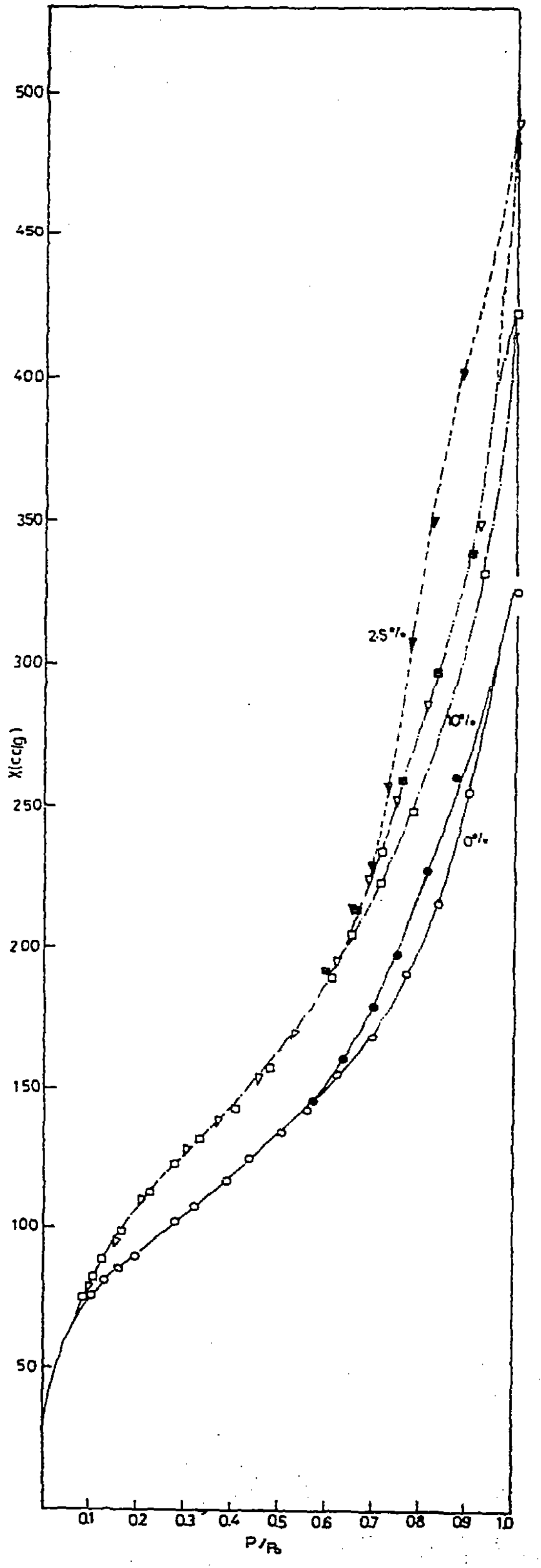


Fig. 7. Adsorption–desorption isotherms of nitrogen on pure silica gel and silica gel containing polyglycol 400 heated at 550°C.

TABLE 1

Surface characteristics of pure and polyglycol 400 containing silica gel and their thermal dehydration products between 110 and 550°C.

Sample	S_{BET} ($m^2 g^{-1}$)	C-BET const.	S_t ($m^2 g^{-1}$)	S_w ($m^2 g^{-1}$)	S_n ($m^2 g^{-1}$)	S_n/S_w	V_p (ml g^{-1})	r_h (Å)	Water content (%)
$SiO_2$110—0%	519	121	520	285	235	0.82	0.7573	15	7.89
$SiO_2$110—2.5%	343	76	325	184	154	0.84	0.4718	15	5.63
$SiO_2$110—10%	299	64	280	97	200	2.06	0.3880	5	4.83
$SiO_2$200—0%	593	121	590	270	323	1.20	0.8319	15	5.89
$SiO_2$200—2.5%	346	126	370	192	154	0.80	0.5587	15	5.41
$SiO_2$200—10%	310	53	310	167	162	0.97	0.5153	5	4.43
$SiO_2$300—0%	346	126	360	194	152	0.78	0.4451	15	4.73
$SiO_2$300—2.5%	516	39	500	253	263	1.04	0.7962	15	3.70
$SiO_2$300—10%	447	39	450	184	263	1.43	0.6138	15	3.31
$SiO_2$400—0%	333	131	365	195	138	0.71	0.5556	15	2.89
$SiO_2$400—2.5%	450	37	460	278	172	0.62	0.7713	15	2.11
$SiO_2$400—10%	413	34	385	212	201	0.95	0.6518	15	1.86
$SiO_2$550—0%	330	66	320	288	183	0.64	0.5069	15	0.98
$SiO_2$550—2.5%	402	31	400	242	160	0.66	0.7589	15	0.76
$SiO_2$550—10%	402	31	400	167	163	0.98	0.6594	15	0.39

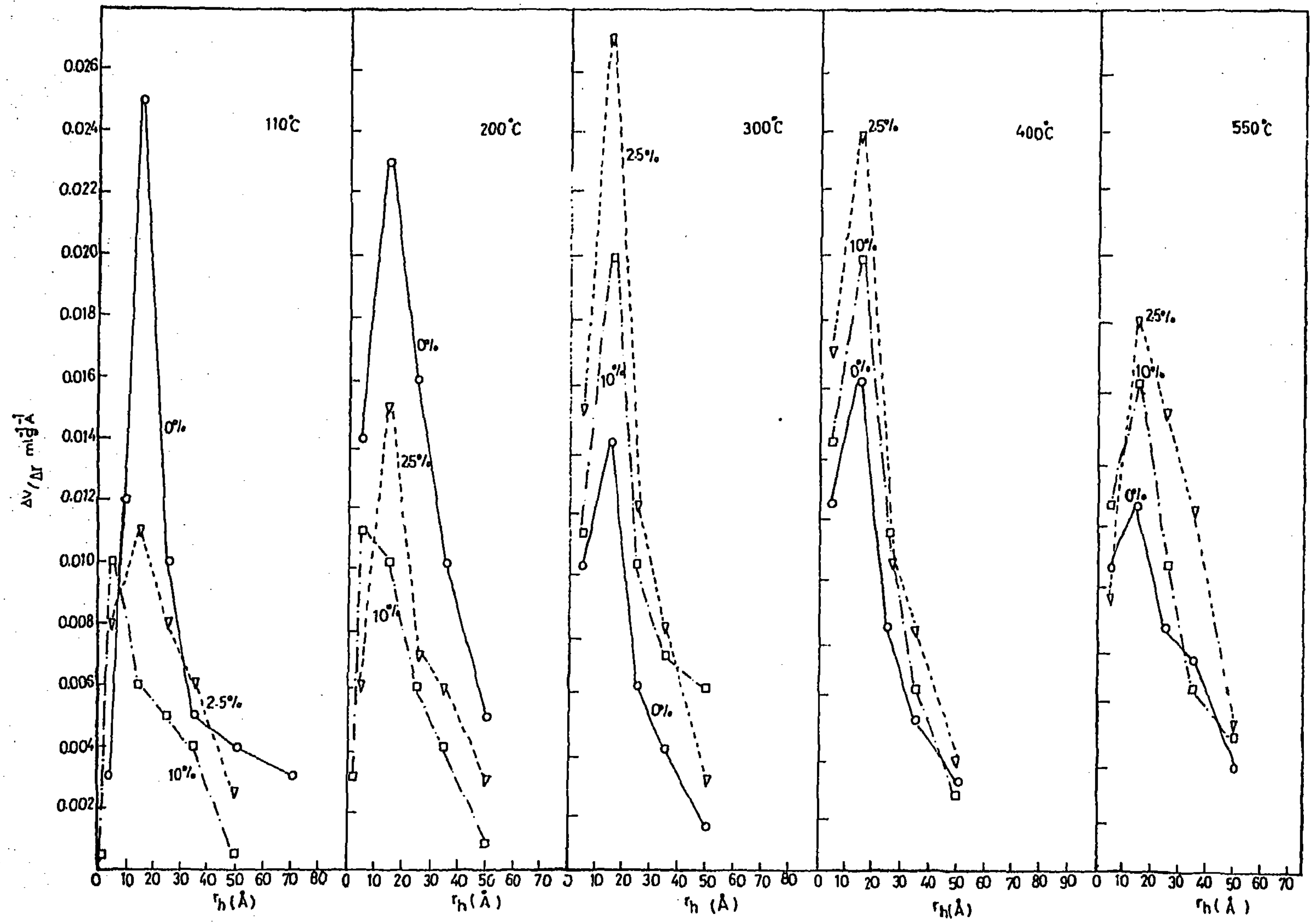


Fig. 8. Pore size distribution curves for pure silica gel and silica gel containing polyglycol 400 and their thermal products between 110 and 550°C.

curves in Fig. 8 were determined from nitrogen adsorption data where suitable t-curves [18–20] could be employed. The samples were analysed by the corrected modeless method [21], using a computer program [22] written in Fortran IV language for an IBM 1130 computer. The analysis was continued to the point of enclosure of the hysteresis loop, assuming a cylindrical pore shape. From the pore analysis cumulative areas S_w ($m^2 g^{-1}$), representing areas located in wide pores, were computed. Thus the areas located in narrow pores S_n ($m^2 g^{-1}$), can be readily obtained by difference from the total area S_{BET} or S_t values. The S_n/S_w ratio, as well as values of total pore volume V_p and mean hydraulic radius $\bar{r}_h$ are also summarized in Table 1.

N_2-Isotherms in Fig. 3 for pure and polyglycol-containing silica gels dried at 110°C reveal clearly that inclusion of polyglycol 400 in the precipitated silica gel is associated with a marked decrease in the nitrogen uptake over the whole range of P/P^0 and also in the shape of the multilayer region, the effects being more pronounced the higher the polyglycol content. Such effects are evidently demonstrated in the marked decrease noted in the surface parameters S_{BET}, S_w and V_p for the polyglycol containing gel in comparison with the pure gel. The bearing of the inclusion of polyglycol 400 on the surface parameters of precipitated silica gel may be interpreted on the basis of inclusion of the linear oligomer molecules in the matrix of precipitated silica gel, which appears to be associated with a more effective elimination of a good fraction of the wider-dimension pores in the gel matrix, leading to a marked increase in the S_n/S_w ratio, as is clear from the diminution in $\bar{r}_h$ value to 5 Å (Table 1).

Increasing the dehydration temperature from 110° to 200°C has no bearing on the relative positions of N_2-isotherms in Fig. 4. However, while the pure gel displays an increase in $S^{N_2}_{BET}$ and V_p parameters, the two oligomer-containing gels appear to maintain almost the same values for these parameters. Changes in these parameters appear to run parallel to changes in the percent water content (cf. Table 1). Accordingly, the observed increase in $S^{N_2}_{BET}$ for the pure gel may be correlated with the partial loss of water content, thus leaving voids, whereas such dehydration effects appear to be prohibited with the oligomer containing gels, probably due to the increase in the skeletal wall of the gel associated with the inclusion of polyglycol 400 in the gel matrix during precipitation.

Changes observed in $S^{N_2}_{BET}$ and V_p parameters taking place at 300°C appear to be controlled by interfering factors other than the loss in water content. Thermal treatment at 300°C seems to allow the water content in oligomer containing gels to force a passage through the gel matrix leaving voids that contributed to a marked increase in area and pore volume parameters. On the other hand, for the pure gel sample, despite the increased loss in water content, a marked decrease in surface parameters is indicated, probably associated with a marked volume contraction of the gel matrix at a somewhat critical percent water loss.

At higher treatment temperatures viz. 400°C, polyglycol containing silica gel exhibited a more marked decrease in surface area than the pure gel due to the shrinkage of the polyglycol by heating. The shrinkage observed in this investigation was very small if it is compared with that occurring upon heating in air [3–6]. In other words, thermal treatment of oligomer containing gels in vacuo protects them from extensive shrinkage.

On heating at 550°C the phase change from the β to α form start to begin which may be accompanied by an increase in surface area. This increase was counteracted by the dercrease in area caused by the shrinkage of the oligomer. This led to the attainment of apparently stabilized values for the surface area at this temperature.

Replacement treatment of OH^- groups by acid centers versus surface characteristics

Samples of pure silica gel and 10% polyglycol 400-containing gel thermally treated at 110°C were soaked in a series of solutions containing 10% by weight of sodium salts of the anions F^-, I^-, SO_4^{2-}, PO_4^{3-}. For comparison samples of pure and 10% polyglycol containing gels were soaked in pure bi-distilled water. Drying of the different samples was carried out at 110°C and nitrogen isotherms at -195°C on the samples were determined (Figs. 9a, b, c, d, e) to investigate the bearing of exchange treatment of OH^- groups with acid-centers on the surface characteristics of the pure and polymer-containing gels.

Figure 9a shows that the uptake of nitrogen on pure and 10% oligomer-containing gels over the mono and multilayer regions is decreased with the replacement of OH^- groups by F^- centers, the effect being more marked with the pure gel. This is clearly demonstrated by the marked downshifts in the nitrogen isotherms on F^- ion-containing samples. Thus inclusion of the polyglycol 400 in silica gel led to a decrease in the population of hydroxyl groups on the surface. However, in the high pressure region where capillary condensation, as an adsorption mechanism, is actively operating, the isotherms rise more steeply, indicative of an increased mesoporosity character. The trends observed in the nitrogen isotherms may be correlated with the following. (i) Aggregation of gel particles into large sized ones, in view of the weakening of the silanol groups by the inductive effect of the F^- ion, appear to develop an interparticulate mesoporous system in contrast to the corresponding gels without F^- substituents. Thus the structure of silica gel, as shown by many authors [11,23,24], is visualized as consisting of a three dimensional network of spherical particles connected at their points of contact. In such a structure the pores are cavities between the packed globules. The size of these globules determines the specific surface area, packing density, pore volume and pore radius. (ii) A decrease in the dipole–quadrupole interaction between the nitrogen molecule and hydroxyl

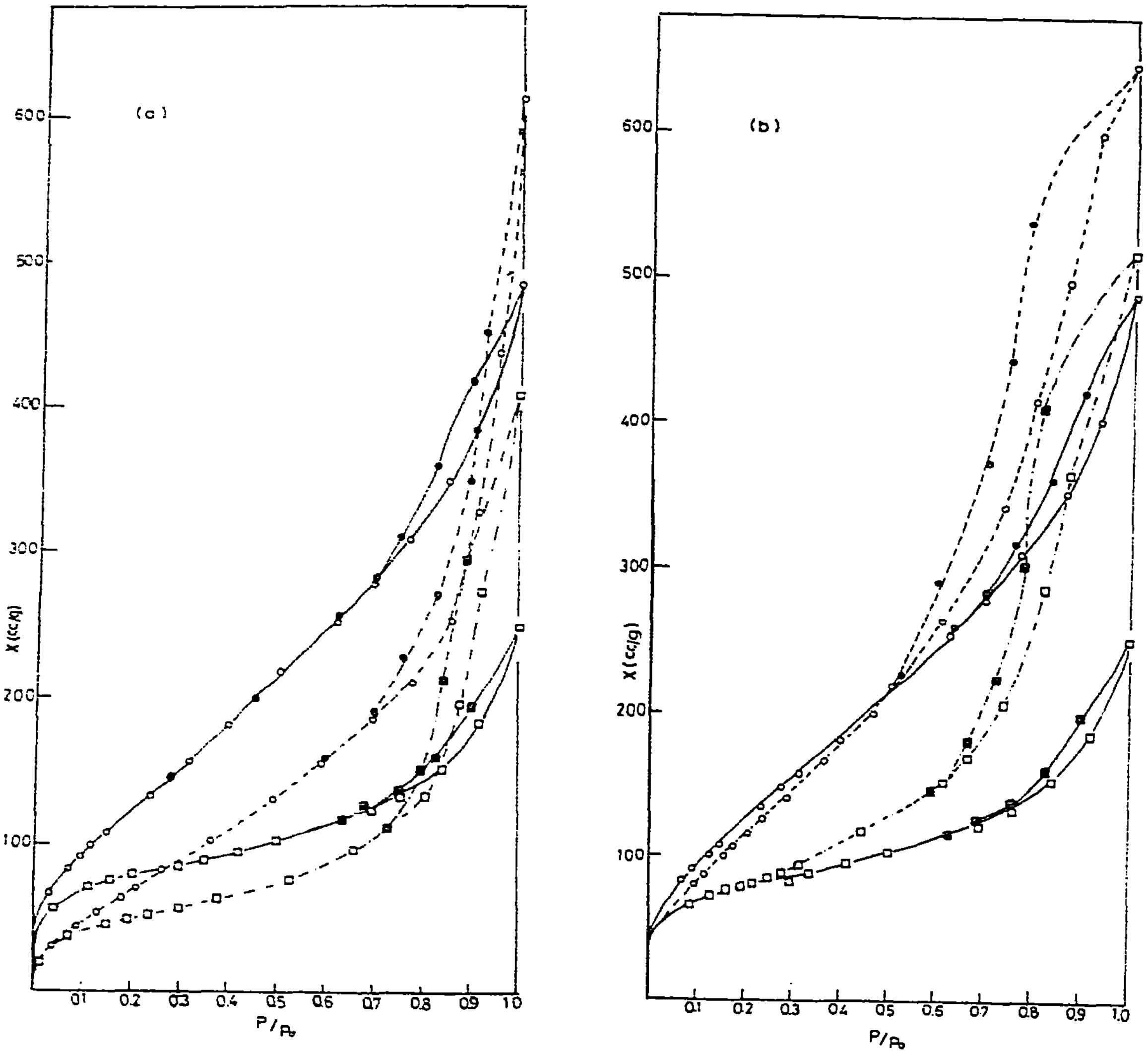
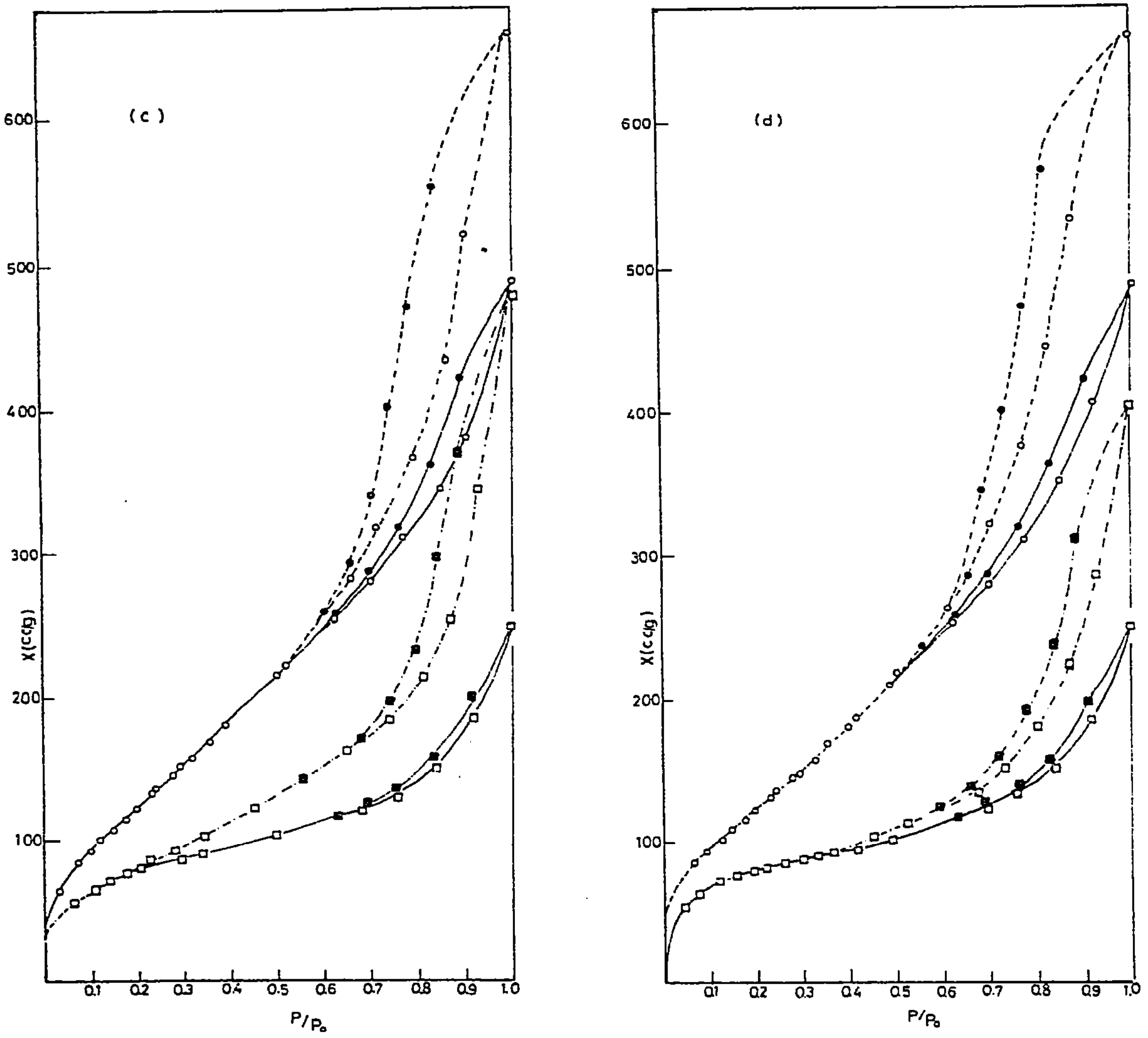


Fig. 9. Adsorption–desorption isotherms of nitrogen on pure silica gel and silica gel containing 10% polyglycol 400 before and after treatment with (a) F^- solution, (b) I^- solution, (c) SO_4^{2-} solution, (d) PO_4^{3-} solution, (e) H_2O. O————O, Silica gel before treatment; O — — —O, silica gel after treatment; □————□, silica gel containing 10% polyglycol 400 before treatment; □–·–□, silica gel containing 10% polyglycol 400 after treatment.

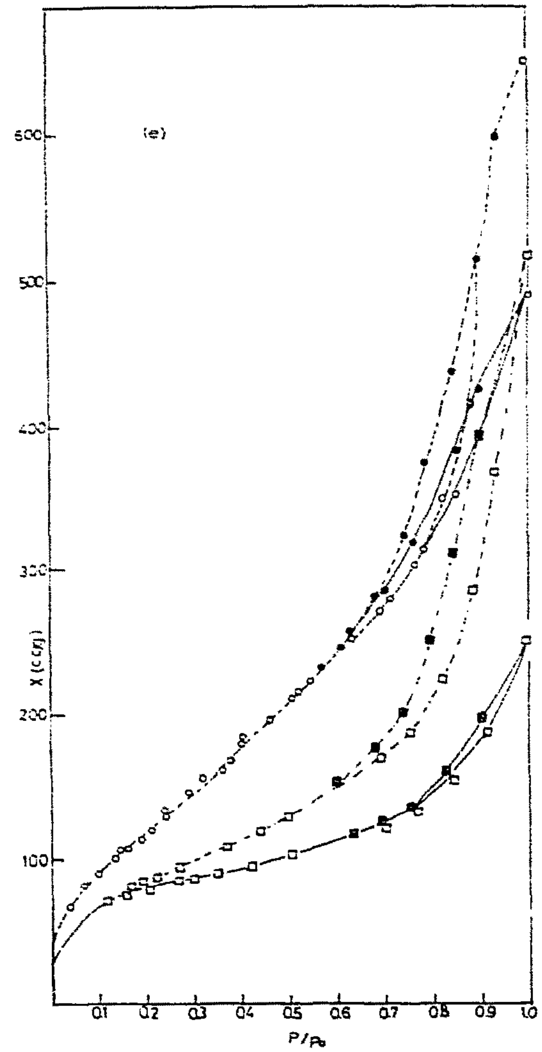
groups due to their replacement with F^- centers.

Figures 9b, c, d reveal that for pure gel samples, the nitrogen uptake over the mono and multilayer regions is but slightly decreased with replacement of OH^- groups with an I^- ion which has a much less inductive effect than the F^- ion (cf. Fig. 9b), whereas it is quite reproduced with the replacement treatment of OH^- groups by the divalent (SO_4^{2-}) and trivalent (PO_4^{3-}) acid-centers (cf. Figs. 9c, d). However, the high pressure hysteresis loops indicated in Figs. 9b, c, d invariably display the marked development of a mesopore system in samples subject to replacement treatment. Nitrogen



isotherms on 10% polyglycol containing gel samples prior and after replacement treatment, invariably display reproduction of nitrogen uptake over the monolayer region only. Departure of the isotherms takes place at intermediate and high pressure regions, whereby adsorption is considered to proceed via multilayer building and capillary condensation mechanisms; the isotherms on the acid-center containing samples fall higher with the development of large-sized high pressure hysteresis loops. Such effects may be correlated with the development of a large volume system of mesopore pores upon aggregation of the gel particles to the extent that it allows more multilayer building followed by marked capillary condensation. In general, the least aggregation for the gel particles is obtained in the case of the PO_4^{3-} substituent due to its bulky size, and the highest for the I^- substituent (cf. Figs. 9b, c).

The effect of rehydration on pure and 10% polyglycol containing silica gel was shown in Fig. 9e from which it is clear that no upshift in the nitrogen isotherm for the pure gel was observed up till $P/P_0 \sim 0.7$ whereas, for 10% polyglycol containing silica gel the upshift in N_2-isotherms started at $P/Po \sim 0.16$.This behaviour reflects the ability of the polymeric silica to rehydrate better than the pure gel, which in turn enhances the dipole–quadrupole interaction between nitrogen molecules and hydroxyl groups.



REFERENCES

1 D. Basmadjian, C.N. Fulford, B.I. Parson and D.S. Montgomery, J. Catal., 1 (1962) 547.
2 A.M. Youssef, J. Colloid Interface Sci., 54 (1976) 447.

3 T.M. El-Akkad and A.M. Kholil, J. Surf. Technol., 13 (1981) 369.

4 (a) T.M. El-Akkad, J. Colloid Interface Sci., 78 (1980) 100,
(b)T.M. El-Akkad, J. Colloid Interface Sci., 80 (1981) 300.

5 T.M. El-Akkad, J. Colloid Interface Sci., 80 (1981) 606.

6 T.M. El-Akkad, J. Appl. Chem. Biotechnol., 30 (1980) 497.

7 C. Okkerse and J.H. de Boer, Proc. 4th Int. Symp. React. Solids, Amsterdam, 1960, p. 240.

8 D. Dollimore and G.R. Heal, J. Appl. Chem., 12 (1962) 445.

9 R. Yu Sheinfain and I.R. Neimark, Kinet. Catal., 8 (1967) 370.

10 D.V. Tarasova, V.A. Dzisko and M.A. Guseva, Kinet. Catal., 9 (1968) 929.

11 C. Okkerse, Physical and Chemical Aspects of Adsorbents and Catalysts, Academic Press, New York, 1970, p. 214.

12 J.V. Smith, (Ed.), X-Ray Powder Data, File and Index to the X-ray data File, ASTM. Philadelphia, 3, 1961.

13 R.I. Razouk and A.S. Salem, J. Phys. Chem., 52 (1948) 1208.

14 F. Singer, Z. Elektrochem., 32 (1926) 385.

15 S. Brunauer, L.S. Deming, W.E. Deming and E. Teller, J. Am. Chem. Soc., 62 (1940) 1723.

16 S. Brunauer, P.H. Emmett and E. Teller, J. Am. Chem. Soc., 60 (1938) 309.

17 D.M. Young and A.D. Crowell, Physical Adsorption of Gases, Butterworths, London, 1926, p. 108.

18 R.Sh. Mikhail, N.M. Guindy and S. Hanafi, Egypt J. Chem. Special Issue Toury, (1973) 53.

19 B.C. Lippens, B.G. Linsen and J.H. de Boer, J. Catal., 3 (1964) 32; J.H. de Boer, B.G. Linsen and Th.J. Osinga, J. Catal., 4 (1965) 643.

20 J.D. Carruthers, P.A. Cutting, R.E. Day, M.R. Harris, S.A. Mitchell and K.S.W. Sing, Chem. Ind., (1968) 1772.

21 S. Brunauer, R.Sh. Mikhail and E.E. Bodor, J. Colloid Interface Sci., 24 (1968) 451.

22 R.Sh. Mikhail, S.A. Selim and A. Goned, J. Chem. ARE, 18 (1975) 5.

23 E. Manegold, Kolloids Z., 96 (1941) 1860.

24 E.A. Leonter and V.M. Lukyanovic, Dokl. Akad. Nauk SSSR, 103 (1955) 1039.