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Further Studies of the Sorption of Ethylamine on Silica Gels

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Adsorption–desorption isotherms of ethylamine at 290° K on silica gels have been determined. Gels of surface areas ranging from 160 to 840 m^2/g and with varied pore characteristics were used. Detailed studies were made of hysteresis loops and abnormal low-pressure hysteresis effects related to slow desorption of ethylamine through rings of tightly held molecules at narrow regions of pores from 35 to 38 Å average diameter.

The pattern of the ethylamine adsorption isotherms, shown by gels containing preadsorbed water, was affected by (i) the amount of preadsorbed water, from 13.0 to 66.7 mg/g and (ii) the time of exposure to water vapor during preadsorption, from 5 to 10 min or 12 hr. It is suggested that these differences are connected with slow rearrangements of the adsorbed water on the gel surface.

Rates of ethylamine desorption were measured on a decimilligram model thermal balance at fixed temperatures from 160° to 220°. Desorption activation energies for 240° and 350° gel surfaces lay between 18 and 21 kcal $mole^{-1}$ for surface capacities from 1.0 to 8.0 mg/g.

INTRODUCTION

In a previous paper (*1*) the interaction of ethylamine on silica and silica xerogel surfaces was described from studies of adsorption isotherms between 275° and 363° K. Isosteric heats of adsorption were measured for surface coverages from one-tenth up to one monolayer. Thermal dehydration of gels up to 1000° had a considerable effect on the subsequent pattern of ethylamine adsorption.

The study has now been extended to include an examination of the adsorption process which takes place up to one-tenth of a monolayer. Activation energies of desorption (*2*) have been measured from 160° to 220° in this range of coverage.

Also, detailed adsorption–desorption isotherms were obtained with silica and silica gels of quite different surface characteristics than those used previously (*1*). The nature of the hysteresis loop has been examined closely and these experiments used to indicate the importance of pore phenomena in influencing the pattern of the adsorption–desorption process.

Isotherm results have been obtained for the adsorption of ethylamine on gels having various amounts of preadsorbed water, equilibrated for 5–10 min and 12 hr.

EXPERIMENTAL

Materials. Davison 923 chromatographic grade silica gel was used as described previously (*1*). Its surface area was 630 m^2/g (BET; N_2; −196°) and lump density 1.145 g/cc. The particle size range was 75–150 μ. Materials were presented by Joseph Crosfield and Sons, Ltd., with the following properties:

(i) "Microporous Sorbsil" silica gel: Surface area (BET; N_2; −196°), 730 m^2/g; lump density, 1.217 g/cc; particle size range, 75–150 μ.

(ii) "Macroporous" silica gel: 215 m^2/g; 0.336 g/cc; 75–150 μ.

(iii) "High Surface Area" silica gel. 840 m^2/g; 1.120 g/cc; 500–2000 μ.

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(iv) "Neosyl FX" pure silica: 690 m^2/g; 0.258 g/cc; 40–100 μ.

Lump densities were measured by immersion in mercury (*3*) after heat-treatment at 240° for 3 hr. Materials (i), (ii), and (iii) were shown by chemical analysis to contain iron up to 25 ppm as the principal impurity.

Ethylamine (99.0%-pure BDH) was purified as before (*1*). Water used in adsorption studies was deionized and then triply distilled. Before use, ethylamine was outgassed three times in the vacuum apparatus. Nitrogen (>99.9%) and helium (99.8%) were used in the highest cylinder purity obtainable (British Oxygen Co.) When these were used as carrier gases in the desorption-rate experiments, they were purified further by passage through a vertical column (50.0 × 3.0-cm internal diameter) packed with alternate layers of self-indicating silica gel and calcium chloride, prior to admission to the saturation chamber.

Apparatus and method. Glass bags were used as sample containers in the static adsorption system already described (*1*).

Rates of desorption were measured on a Stanton model thermal balance, type HT-D. This had a sensitivity of 0.1 mg and a total chart span of 10 mg. The instrument had a bifilar platinum-rhodium furnace capable of 1400°. It was modified to include (i) a proportionating control unit to give temperature control to ±0.05° up to 250°; (ii) a direct sample temperature thermocouple connected via compensated leads through separate cold junctions (0°) to a recording potentiometer (Honeywell-Brown) of 2-mV full-scale deflection; and (iii) a 28-mm internal diameter mullite furnace tube with top outlet.

A quartz bucket was used with the thermal balance to contain 0.5–1.0 g samples. No adsorption of ethylamine was detected on this bucket nor on the ceramic support assembly. An all-glass flow system was attached to the balance. Its essentials included capillary flow meters, calibrated 30–120 ml/min, carrier gas and ethylamine purification columns.

RESULTS

Complete adsorption–desorption isotherms were determined at 290°K on Davison 923 gel pretreated at 240° for 3 hr, and also at 500°, 600°, 700°, 800°, and 900° for 20 hr each. All samples were further outgassed in the static adsorption apparatus as described (*1*), prior to isotherm measurement. On first exposure to ethylamine there was a large amount of amine adsorption at a fast rate at low rela-

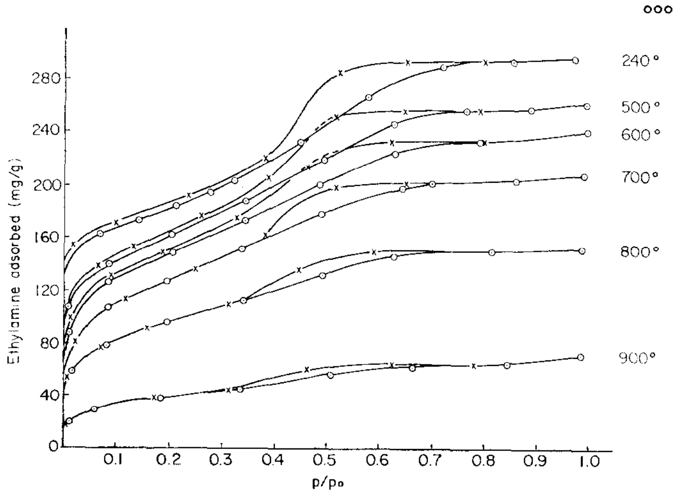

FIG. 1. Ethylamine adsorption–desorption isotherms at 290°K on silica gels heat-treated (20 hr) at various temperatures.

TABLE 1

PHYSICAL PROPERTIES AND ETHYLAMINE ADSORPTION CAPACITIES OF DAVISON 923 GEL

Dehydration temperature (°C)	Hydroxyl group concentration (μmole/m^2)	Surface area (m^2/g)	Lump density (g/cc)	Monolayer capacity (mg amine/g gel)	Saturation capacity ($p/p_0 \sim 1$) (mg amine/g gel)
240°	9.6	630	1.1448	150.0	299.0
500°	4.0	615	1.1931	132.7	264.0
600°	3.0	545	1.2449	122.8	244.0
700°	2.1	485	1.3108	106.3	211.0
800°	2.0	360	1.4348	74.0	156.0
900°	1.9	160	1.6839	29.6	74.0

tive pressures by all samples. The monolayers were completed at relative pressures of 0.022 (240°), 0.057 (500°), 0.072 (600°), 0.080 (700°), 0.060 (800°), and 0.065 (900°). Steady compression of the hysteresis loop with increase in dehydration temperature was observed. For 240°, 500°, and 600° gels noncoincidence of the adsorption and desorption isotherms was noted below relative pressures of about 0.75. Coincidence of adsorption and desorption isotherms below relative pressures of 0.35 was found for 700°, 800°, and 900° gels (Fig. 1).

For these materials, hydroxyl group concentrations (*1*) BET surface areas, and lump densities were determined; they are given in Table 1. This table also shows the amine adsorption capacities at monolayer completion and at saturation.

Monolayer ethylamine capacities were determined from BET plots (Fig. 2). In

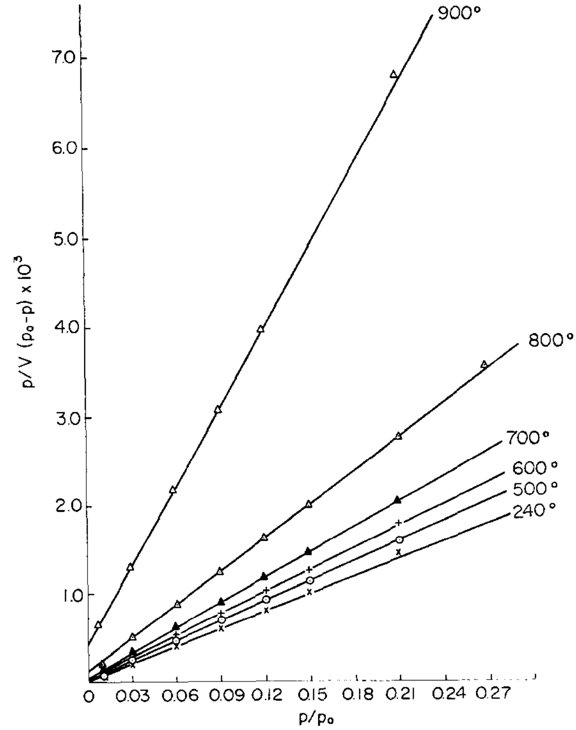

FIG. 2. BET plots of ethylamine adsorption on heat-treated silica gels.

all cases, this equation held from $p/p_0 =$ 0.01 to 0.25.

Table 1 shows that between 240° and 500° there was very little loss in surface area of the gel. Above 500°, there was a steady loss which increased in the region of 700° and continued rapidly to 900°. The hydroxyl group concentration fell considerably between 240° and 500° and thence more slowly to 700°. Above 700° there was only a slight decrease in hydroxyl group concentration. Both monolayer and saturation ethylamine capacities fell fairly steadily with increase in dehydration temperature up to 700° and then more rapidly to 900°.

The Nature of the Hysteresis Loop

A series of experiments was carried out with the 240° gel to obtain more details of the adsorption hysteresis. In particular, data were required to decide on the cause of the noncoincidence of the adsorption and desorption isotherms beyond the normal point of closure of hysteresis loops, i.e., below $p/p_0 = 0.35$–0.40. Later, the phenomenon found in this pressure region is referred to as the "subhysteresis" loop. It was important to find where, and under which conditions, subhysteresis effects were initiated. Hence, starting with a bare surface, detailed adsorption–desorption isotherms were determined up to and away from various equilibrium-adsorbed amounts of gas over the p/p_0 range 0 to 0.583 at 290°K. The results are summarized in Table 2. The subhysteresis amount is given by the difference in uptake of the desorption and adsorption isotherms at $p/p_0 =$ 0.05.

Adsorption equilibrium times were normally 60 min with desorption times less than 45 min. Extensions of these times to several hours made no difference in the amounts adsorbed at equilibrium nor to the subhysteresis amounts. Table 2 indicates that the noncoincidence is associated with desorption relative pressures from 0.368 to 0.408, with final adsorbed amounts about 220 mg/g.

As a test of the tenacity by which the ethylamine causing the subhysteresis was held to the 240° gel, large quantities of amine were preadsorbed at 290°K with $p/p_0 = 0.99$. Then controlled quantities were left on the gel by careful evacuation. Subsequently, complete adsorption–desorption isotherms were determined on these samples (Fig. 3). With 113.2 mg/g preadsorbed, the adsorption and desorption isotherms coincide below $p/p_0 \sim 0.25$, while part of the subhysteresis loop is visible from $p/p_0 = 0.25$ to 0.35. (Isotherm B). For a preadsorbed amount of 73.3 mg/g there was noncoincidence of isotherms from $p/p_0 \sim 0.8$ to 0 (Isotherm A).

TABLE 2
TOTAL AND SUBHYSTERESIS AMOUNTS OF ETHYLAMINE ADSORBED WITH 240° GEL AT 290°K

Total adsorbed amount (mg amine/g gel)	Final equilibrium relative pressure (p/p_0)	Subhysteresis amount (mg amine/g gel) ($p/p_0 = 0.05$)
180	0.205	0.0
214	0.368	0.0
220	0.408	~1.0
234	0.445	3.0
249	0.495	3.0
266	0.555	4.5
273	0.583	5.5

To supplement these studies, a series of gels with large differences in pore structures was investigated. All isotherms determined at 290°K on 240° gels showed the subhysteresis loop. The noncoincidence amounted to about 3 to 4 mg/g at $p/p_0 =$ 0.05 in all cases. "Macroporous," "High Surface Area," and "Neosyl FX" showed noncoincidence on desorption from $p/p_0 =$ 0.85 to 0, "Microporous" from 0.45 to 0. Treatment of the Microporous gel at 700° for 20 hr gave the adsorption-desorption isotherm C of Fig. 4. This shows an amine adsorption of 33.0 mg/g at $p/p_0 = 0.05$ and a total adsorbed amount of 51.0 mg/g at 0.99. The adsorption and desorption isotherms coincide over the whole p/p_0 range. Following dehydrations at 800° and 900° for 20 hr, the Microporous gel gave a total amine adsorption of 9.5 mg/g ($p/p_0 = 0.97$) and 5.6 mg/g (0.99), respectively. Both

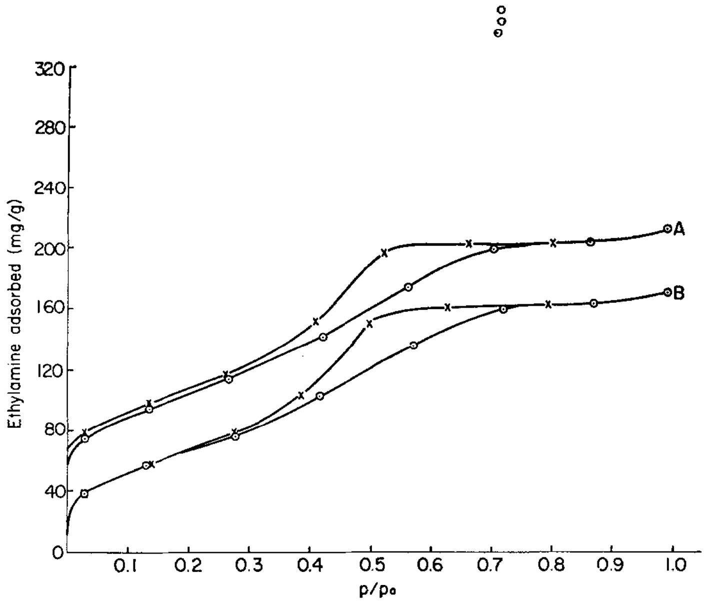

FIG. 3. Ethylamine adsorption-desorption isotherms on silica gels at 290°K with (A) 73.3 mg/g and (B) 113.2 mg/g ethylamine preadsorbed.

amounts were readily desorbed within 5 min following pressure reduction.

In an attempt to differentiate between inter- and intraparticle adsorption with these materials, Neosyl FX pure silica was compacted at 200 kg/cm^2 into 0.5 × 13-mm diameter pellets. The 290°K isotherm on 240° pellets is shown in Fig. 4(A). There

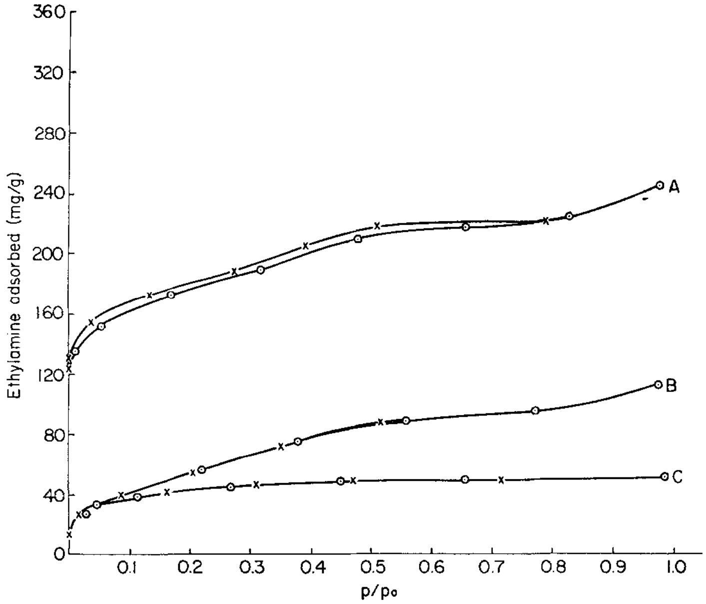

FIG. 4. Ethylamine adsorption-desorption isotherms (290°K) on silica gels with pore-structure variations: A, Neosyl FX pellets (240°); B, Neosyl FX pellets (240°) with 122.0 mg/g ethylamine preadsorbed; C, Microporous (700°) powder.

is an initial large adsorption of 154.5 mg/g at $p/p_0 = 0.05$ and a saturation adsorbed amount of 247.0 mg/g ($p/p_0 = 0.98$). There is noncoincidence of adsorption and desorption isotherms from $p/p_0 \sim 0.8$ to 0. The isotherm shows the same characteristics as that obtained on pure, powdered Neosyl FX. The only difference was an overall drop in amine adsorption on the compacted material of 22.0 and 51.0 mg/g at $p/p_0 =$ 0.05 and 0.98, respectively. A complete isotherm was measured with fresh (240°) Neosyl FX pellets at 290°K which had 122.0 mg ethylamine/g preadsorbed. Figure 4 B shows complete coincidence of adsorption and desorption isotherms in the subhysteresis range and a very small hysteresis loop.

Preadsorption of Water

Controlled amounts of water vapor were adsorbed at 290°K on 923 gel after activation at 240° for 3 hr. The subsequent ethylamine adsorption pattern was studied. Water vapor was allowed to contact the sample in the adsorption chamber at a pressure of 20 mm Hg for periods from 5 min to 12 hr. Controlled amounts were left on the gel by careful pumping out.

After 5–10 min gel/water equilibration times, all the adsorbed water was desorbed within 10 min. After 12-hr equilibration up to 1.5-hr desorption under 10^{-5} mm Hg vacuum was required to remove all but 13 mg water/g gel. Figure 5 shows ethylamine adsorption isotherms determined on 923 samples which held various amounts of preadsorbed water from 66.7 to 13.0 mg/g. The water/gel equilibration times were either 5 min or 12 hr. In each case the time of exposure to water vapor, as well as the quantity of water preadsorbed, had a considerable effect on the form of the isotherm. Ethylamine/gel equilibration times for 66.7 mg/g preadsorbed water were 45 min up to $p/p_0 \sim 0.78$, 255 min (0.78–0.87), and

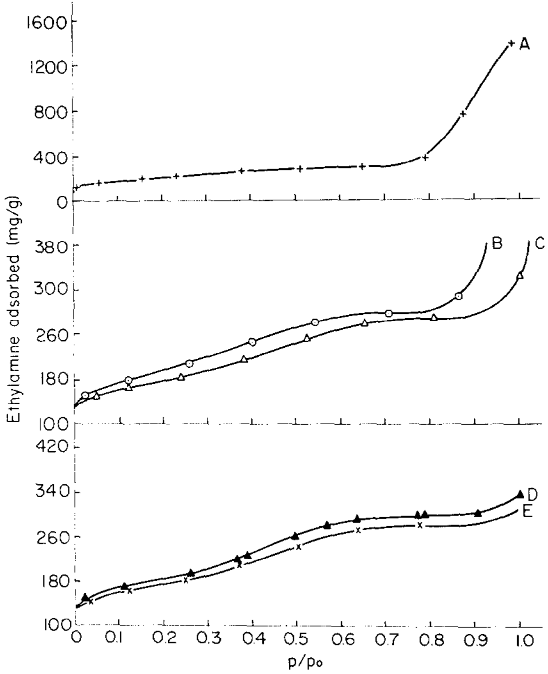

FIG. 5. Ethylamine adsorption isotherms at 290°K on 240° gels. Showing effects of preadsorbed water: A, 66.7 mg water/g gel preadsorbed; water/gel equilibration time, 12 hr. B, 28.4 mg water/g gel; 5 min. C, 29.2 mg water/g gel; 12 hr. D, 13.0 mg water/g gel; 5 min. E, 13.0 mg water/g gel; 12 hr.

15 hr (>0.87). As the amount of preadsorbed water was decreased these times decreased slightly. At the highest relative pressures of ethylamine the adsorbed layer achieved a "liquid-like" appearance which was more marked as the quantity of preadsorbed water was increased and as the water-gel equilibration times were decreased.

Desorption-Rate Studies

Gel 923 was heat-treated at 240° for 12 hr on the thermal balance. Amine adsorption times of 10–20 min were used to give known adsorbed amounts from 5 to 10 mg/g at 160° and 220°. The effect of carrier-gas flow rate on the subsequent rate-of-desorption pattern was examined as before (*2*). At both 160° and 220°, the rate of desorption of an initial adsorbed amount of 5.0 mg/g was independent of nitrogen carrier-gas flow rate from 50 to 90 ml/min. From 90 to 120 ml/min the rate of desorption was affected very slightly at 160° but more so at 220°. At 220° the rate of desorption became much less influenced by flow rate as the initial surface capacity was decreased in the series 4.0, 2.0, 1.0 mg/g, while at 160°, initial capacities of 7.5 and 10.0 mg/g gave a slightly more flow-rate-dependent rate-of-desorption pattern above 90 ml/min than that found with capacities of 5.0 mg/g. As a result of these experiments, rates of desorption were studied with a carrier-gas flow rate of 60 ml/min and activation energies were calculated, wherever possible, with surface capacities of no more than 8.0 mg/g.

The time of heat-treatment of the gel in the activation procedure at 240° influenced the ethylamine rate-of-desorption curve obtained. On heating at 240°, after initial rapid weight loss over 3 hr, the gel lost an additional 2.0 mg/g over the next 8 hr, and although the material appeared to be weight constant at this stage, subsequent

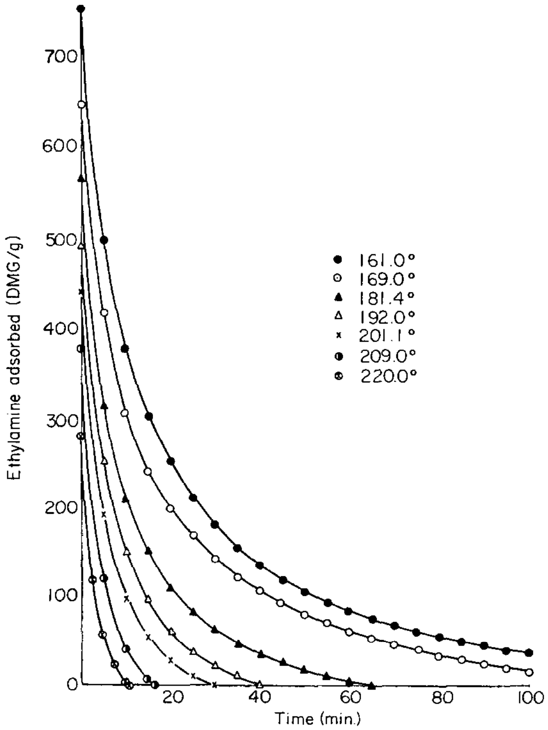

FIG. 6. Rates of desorption of ethylamine at 161° to 220° from 240° (12 hr) gel. Adsorption time, 15 min.

heating for a total of 72 hr gave a further loss of 1.0 mg/g. For these desorption-rate studies, a standardized heat-treatment time of 12 hr was usually adopted, prior to ethylamine adsorption on the gel.

Rates of desorption were measured at a series of fixed temperatures in the range 160°-220° for 240°, 350°, and 900° (20 hr) surfaces. Figure 6 shows the results obtained for the 240° surface when an adsorption time of 15 min was used. From 160° to 220° there was a decrease in the quantity of ethylamine adsorbed initially. Desorption was rapid at high coverages, falling in rate as the surface ethylamine concentration was decreased. This effect was most noticeable at the lower desorption temperatures. The curves of the desorption rate at 220° and 209° level out beyond 100 min without achieving the initial steady value of the gel weight prior to ethylamine adsorption. Plots of $\log_{10}$ (rate of desorption) against $\log_{10}$ (weight of ethylamine retained by gel) were excellent straight lines with a slope of unity over the whole temperature range.

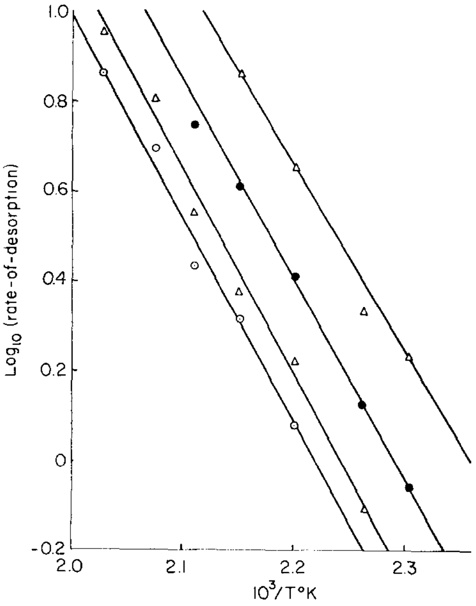

FIG. 7. Arrhenius plots of ethylamine desorptio rates from 240° gel. Adsorbed amounts: ⊙, 1.0 m g; ⊡, 2.0 mg/g; ⊕, 4.0 mg/g; ◇, 8.0 mg/g.

Figure 7 shows $\log_{10}$ (rate of desorption) against $1/T$° K for a series of fixed amounts of ethylamine retained by the gel. From the slopes of these lines the activation energy of desorption, Table 3, was calculated in the usual manner.

TABLE 3
DESORPTION ACTIVATION ENERGIES FROM 240° GEL

Amount of ethylamine retained by gel (dmg/g)	Energy of activation ±0.4 (kcal mole^{-1})
10	20.6
20	20.9
40	20.3
80	18.8

It was found that at desorption temperatures above 180° the final stable weight of gel was less than that originally recorded for the 240° surface. This feature is indicated by Fig. 6, where the first five curves are shown to penetrate the time axis before leveling out. The weight deficits thus found are shown in Table 4. Such observations were made previously in studies of ammonia desorption (*2*) where the phenomena was shown experimentally to be related to a "catalytic" dehydration of the gel by the adsorbed gas with subsequent loss of water molecules from the surface.

TABLE 4
DEHYDRATION PARAMETERS OF 240° GEL, ON DESORPTION AT VARIOUS TEMPERATURES

Desorption temperature (°C)	Initial amount of adsorbed ethylamine (dmg/g)	Desorption time (min)	Loss in weight of gel (dmg/g)
220.0°	281	100	56
209.0°	380	75	50
201.1°	442	100	33
192.0°	491	100	29
181.4°	567	100	22
169.0°	650	100	+17
161.0°	750	100	+37

On 350° gel the amount of ethylamine adsorbed initially showed a slight increase in initial amounts over those in Fig. 7. The rate-of-desorption patterns from 160° to 220° followed a broadly similar path to those in Fig. 6 without showing the apparent dehydration above 180°. Only a small weight deficit, 0.1 mg/g, could be attributed to dehydration at 222°. On 900° surfaces no dehydration effect was detected from 160° to 220°. Rate of desorption vs. weight retained plots followed simple first order kinetic patterns for 350° and 900° xerogels at all desorption temperatures. Desorption activation energies were determined on 350° gel as 19.8 ± 0.5 kcal mole^{-1} with surface capacity, 3.0 mg/g; and 20.8 ± 0.5 kcal mole^{-1}, surface capacity, 6.0 mg/g. For the 900° gel the desorption activation energy at a coverage of 1.0 mg/g was 15–18 kcal mole^{-1}.

DISCUSSION

The results of the various experiments in the subhysteresis loop studies may indicate that the phenomenon is related to pore structure. After heat-treatment at 700° and above the subhysteresis loop cannot be detected. Treatment above 700° causes considerable changes in the surface area, pore-size distribution, and lump density of silica xerogel (*4*). Bulk sintering commences in this temperature region accompanied by rapid densification and pore collapse. With samples modified by heating under 700°, however, the subhysteresis loop occurs below relative pressures of about 0.4. Neither temperature of isotherm measurement (from 273.8° to 298°K) nor time of desorption equilibrium had any significant effect on this phenomenon.

The pore statistics of all gels used in this study were computed from nitrogen adsorption measurements by the method of Cranston and Inkley (*5*). These results (*6*) showed that the large majority of pores in 923 gel lay in the region 20–40 Å diameter and that at ethylamine relative pressures from 0.40 to 0.44, pores from 35 to 38 Å diameter were being filled. A plot of pore volume against temperature for pores of 37.5-Å diameter showed that this volume rapidly diminised in 923 gels treated above 600°. However, pore distribution data for the Microporous and Macroporous gels showed that both had appreciably smaller numbers of pores of 37.5-Å diameter than the 923 gel which had been heated at 700°. Yet both Microporous and Macroporous materials gave a subhysteresis loop while the 700° gel did not. These differences may be due to pore shapes—the isotherms are of different types—and to the absence of appreciable amounts of residual hydroxyl groups on the 700° material.

The hysteresis loops of the ethylamine, and nitrogen, isotherms on 240° and 500° gels do not have any very steep branches. Nevertheless, they most closely resemble the shape of loop designated by de Boer (*7*) as Type E. Pore shapes normally associated with this type include "ink-bottle" pores with narrow short necks or tubular pores with a narrowed body portion at some point. Such pores should fulfill the condition (*7*) $d_n < d_w < 2d_n$, where d_n and d_w are the respective diameters of the narrower and wider parts.

The average pore diameter calculated by the Cranston and Inkley method is a statistical value based on the assumption of cylindrical pores with a closed end. Pores of average diameter 37.5 Å will certainly have narrower and wider regions than this. From the above condition a minimum value for d_n of about 19 Å is indicated, with a maximum about 37 Å. Calculation of the cross-sectional area of an adsorbed ethylamine molecule using Livingston's equation (*8*) leads to a value of 24.8 Å^2, assuming two-dimensional close-packing. Hence, only three ethylamine molecules could readily form one line from wall to wall across the diameter of a narrowed pore section of 19 Å.

It is envisaged that, on adsorption, monolayer coverage proceeds evenly, probably involving hydrogen bond formation of the $N---H—O$ type (*1*) between amine and gel from $\theta = 0.1$ to 1.0 on the 240° and 500° surfaces. As a result the hydrocarbon end group of the amine would become polarized positively. In this condition there is still room in the narrowed pore sections for subsequent molecules to enter on multilayer buildup. However, on desorption at $p/p_0 \sim 0.4$ the last few molecules to leave the pores no longer have sufficient collision energy to desorb normally through narrow sections and become temporarily trapped by the ring of polarization forces induced in the hydrocarbon end group of the adsorbed amine molecules. This type of situation may persist down to the lowest relative pressures when the surface holds only a small fraction of an ethylamine monolayer.

The marked difference in the tenacity of the gels for preadsorbed water after 5-min and 12-hr exposure to water vapor indicates that water molecules rearrange on the gel surface in this time interval. After 5 min exposure the water is all desorbed readily within 10 min. Therefore it is probably present mainly as a physically adsorbed film. After 12-hr contact time, several possibilities arise, two of which may be more likely:

(a) Water molecules become attached to the surface by double hydrogen bonds (*9*), one molecule of water for every two silanol groups (*10*).

(b) Adsorbed water molecules gradually diffuse into fine pores and perhaps form aggregates. Desorption would then be a slow, diffusion-controlled process especially at a temperature of 290°K. Such aggregation would reduce the pore volume of the gel with respect to the subsequent adsorption of ethylamine.

After 12-hr contact time with the large quantity of preadsorbed water, 66.7 mg/g, it is probable that physical adsorption, adsorption through hydrogen bonds and pore condensation are all important to various degrees. Water/gel equilibration times of 5 min had more effect on the shape of the ethylamine isotherms above $p/p_0 = 0.5$, than the 12-hr equilibration times (Fig. 5). Below $p/p_0 = 0.5$, amine adsorption was further reduced following 12-hr equilibration compared with 5-min equilibration and with amine isotherms on untreated samples. After 5-min equilibration, there was a very large rise in the quantity of amine adsorbed above $p/p_0 = 0.5$, which increased as the quantity of water left adsorbed on the gel over 5-min exposure periods was decreased. This feature was less marked after 12-hr exposures, although it still occurred to some degree.

It is suggested that following short gel/water equilibration times, the adsorbed ethylamine molecules displace the physically adsorbed water molecules from surface hydroxyl sites. The water is not desorbed by this displacement but moved aside on the surface, away from amine adsorption centres. Above $p/p_0 = 0.5$, amine and water molecules begin to mix—they are completely miscible in the liquid phase and as more physically adsorbed water is left on the gel, the extent of mixing increases. This is consistent with the high-pressure observations where the adsorbate appeared to be in solution on the gel surface.

After 12 hr water/gel equilibration, the amine adsorption may be inhibited by the presence of hydrogen-bonded water. This water is apparently too strongly attached to surface hydroxyl groups to be displaced by the amine. As a result, there would be a reduction in amine adsorption in the lower pressure regions, as was observed.

A quantitative comparison of isosteric heats of adsorption with energies of activation of desorption is possible when the desorption process is zero order (*11*). In the present experiments the ethylamine desorption rate followed a first order kinetic law. Further, the desorption activation energies were measured at lower surface coverages than the earlier (*1*) isosteric heat measurements, $\theta = 0.1$ to 1.0. However, it is worth noting that the desorption activation energy at θ's < 0.05 lay around 20 kcal mole^{-1}, depending on the surface, and that the extrapolated value for q_{st} in this region is similar.

Rates of desorption at 160–220° from the 240°, 350°, and 900° surfaces were initially very rapid. The flow-rate experiments showed that for above 10 mg/g ethylamine retained, the rate of desorption was transport-controlled for the 240° and 350° materials. For the 900° gel, this region occurred above 2 mg/g ethylamine retained. Overall rates of desorption were faster on the 240° than on the 350° and 900° gels. This is probably due to the amine catalytically dehydrating the 240° surface. Thus, in addition to loss of amine from the surface, an additional weight loss due to water desorption comes into play.

Subsequent to the initial rapid desorption, regions of much slower desorption rate were obtained, particularly on the 350° and 900° gels. This is attributed to stronger amine/gel interactions. In these regions the desorption rate was quite independent of flow parameters. Also, on the assumption that the energy of activation of desorption provides a measure of the energy required to dissociate the amine/gel surface complex, prior to desorption, then strong interaction is also indicated. Lange (*12*) has recently attributed desorption activation energies of water from silica gel of about 10 kcal mole^{-1} to the presence of a doubly hydrogen-bonded species on the surface. On these grounds our earlier assumption (*1*) that below $\theta = 0.1$ the adsorption of ethylamine on silica gel involves a strongly adsorbed ionic species, seems justified. Values of 20 kcal mole^{-1} for desorption activation energies seem too high to be attributed to hydrogen bonding or to pore diffusion phenomena.

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