316. *Adsorption of Organic Bases on Silica Gel, and Heats of Adsorption. Part II.*

By B. P. GYANI.

The adsorption of diethylamine, triethylamine, pyridine, α-picoline and piperidine on silica gel has been measured at 35°. The heats of adsorption have been determined by a tensimetric method. The entropy changes accompanying desorption are similar to those accompanying evaporation of the free liquid.

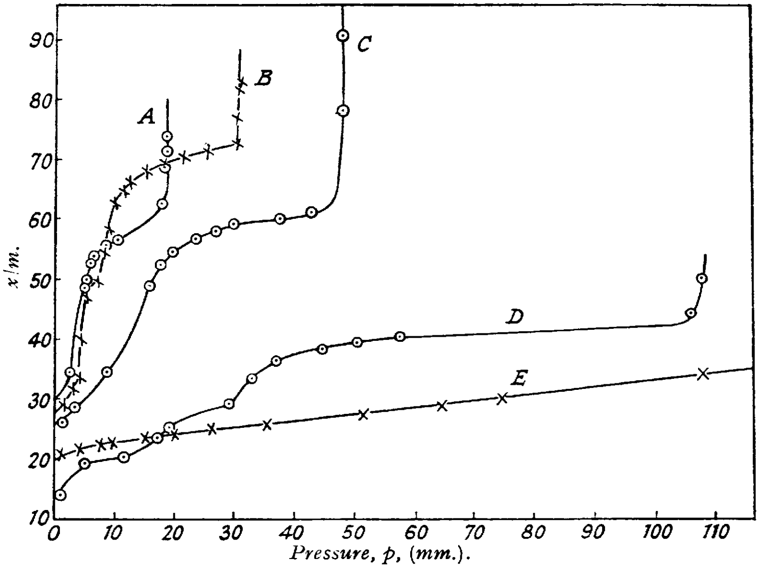
IN a previous paper (*J. Indian Chem. Soc.*, 1949, **26**, 345) measurements of the heat of adsorption of methyl alcohol and its homologues on silica gel have been described. The primary object of the present investigations was to see whether any marked changes in the adsorption isotherms and heats of adsorption are produced when bases are substituted for the alcohols.

EXPERIMENTAL.

The silica gel was prepared by mixing, with vigorous shaking, equal volumes of commercial hydrochloric acid, diluted to *d* 1·05, and commercial sodium silicate syrup diluted with water to *d* 1·12. The resulting sol was allowed to set at about 30°, then cut into small pieces, washed thoroughly, and dehydrated gradually at increasing temperatures. The final desiccation was at 350° in a current of dry air. The gel was about two years old at the time of the measurements. The liquids were purified according to standard methods before use and had satisfactory b. p.s. The gel was evacuated at about 300°, cooled, and flushed several times with the appropriate vapour before the observations were recorded. An oil-pump giving a vacuum of 0·001 mm. was used for evacuating the gel and no attempt was made to improve the vacuum.

FIG. 1.

Adsorption isotherms.



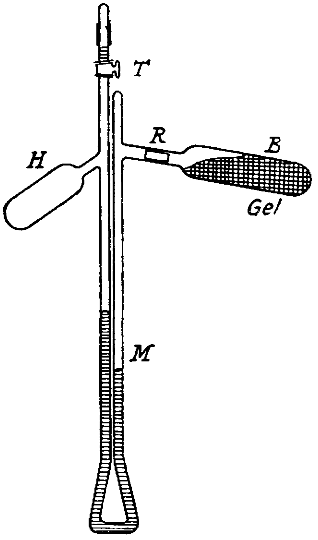
A, α-Picoline; B, pyridine; C, piperidine; D, triethylamine; E, diethylamine.

The adsorption was measured in an apparatus previously described (*J. Physical Chem.*, 1945, **49**, 226). The amounts of adsorption at different pressures of the vapour were measured by noting the increase in the weight of a fixed amount of the gel (about 4 g.) contained in a detachable bulb weighing about 15 g. At half saturation of the gel the amount of adsorption was well over 1 g. in each case. The bulb had a fixed dead space of less than 2 c.c. A vapour having a molecular weight of 100 occupying this dead space at a pressure of 100 mm. would weigh less than 0·001 g. at the temperature of these experiments, so that the error in determining the amount of adsorption was in general less than 0·1%. The pressure of the vapour was measured on a simple mercury manometer. By a short-range telescope pressures were read on a metre scale directly attached to the manometer, with an accuracy of ±0·1 mm. The adsorption bulb was enclosed in an air thermostat whose temperature was kept constant at 35° ± 0·1°.

Fig. 1 shows the plot of the amount of adsorption per g. of the gel, x/m, against pressure p of the vapour. x has been expressed in 10^{-4} g.-mol. of the liquid and p in mm. of mercury. The data plotted refer to desorption only. These isotherms were found to be satisfactorily reproducible. The adsorption isotherms were a little erratic in the beginning but gradually settled down in the neighbourhood of the desorption isotherms except for small regions of hysteresis towards saturation pressures. It is surprising that the isotherms for the different bases are not similar in shape. The simplest isotherm is given by diethylamine which appears to belong to type I described by Brunauer (" The Adsorption of Gases and Vapour," Vol. I, Oxford Univ. Press, 1943, p. 150). The piperidine and α-picoline curves are sigmoid, corresponding to type IV. The remaining two isotherms have a number of distinct loops and correspond to none of the types described by Brunauer. Somewhat similar discontinuities in the adsorption isotherms of alcohols on silica gel have been observed by the author earlier (*J. Physical Chem.*, 1945, **49**, 226).

FIG. 2.

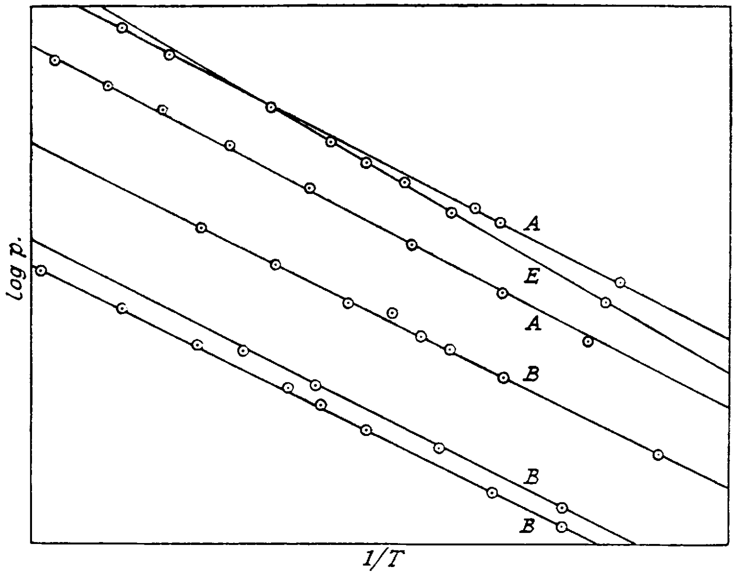
The tensimeter.



Isosteric Heats of Adsorption.—The heats of adsorption on the same sample of the gel were obtained by a tensimeter. The apparatus is shown in Fig. 2. The adsorption bulb containing the gel was sealed to one limb of the manometer *M*. A glass rod placed between two slight constrictions at *R* prevented the gel particles from falling into the manometer during handling. Another small bulb *H* was sealed to the other limb of the manometer. Sufficient mercury was introduced into the apparatus to fill half the manometer on either side. It was then collected into *H* by tilting the apparatus. *B* was then heated to about 300° while the apparatus was being evacuated with an oil-pump. When the evacuation was complete the tap *T* was closed and the bulb allowed to cool. A quantity of the freshly distilled liquid under investigation was introduced into the apparatus. The vapour was rapidly absorbed by the gel, and the process was aided by cooling. The excess of liquid which collected in *B* was heated almost to boiling and kept at that temperature for some minutes to get rid of the gases retained by the gel during heating and evacuation. The excess of liquid was then pumped out, the tap *T* closed, and the mercury returned to the manometer. The manometer on the side of *H* was then fully evacuated, and the apparatus clamped vertically in a large thermostat. The tap was sealed with a few drops of mercury and painted on the sides with molten Faraday cement. The thermostat was maintained at temperatures constant to within 0·1°. Pressures were read as described above in the adsorption experiments.

FIG. 3.

Plot of log p *against* 1/T.



A, α-Picoline ; B, pyridine ; E, diethylamine.

The thermostat was set at different temperatures (room temperature to about 70°) and the pressures of the vapour in contact with the gel at these temperatures were read to the nearest 0·1 mm. After completion of runs at an arbitrarily fixed composition the tensimeter was removed from the thermostat. The mercury was again collected in *H* and a quantity of the vapour was pumped out from the gel to reduce the amount of adsorption. The apparatus was then reset for another run. The value of the adsorption, x/m, was computed by reference to the previously determined isotherms at 35°.

Reproducibility in these experiments was good. Different runs at a fixed amount of adsorption rarely showed a pressure difference of 1 mm. at the same temperature. The measurements were performed with different quantities of the gel in the bulb and some of the measurements were checked by a duplicate apparatus. One can therefore be sure that the results were not vitiated owing to presence of the dead space inside the apparatus (which at any rate was small) or by non-uniformity of the gel.

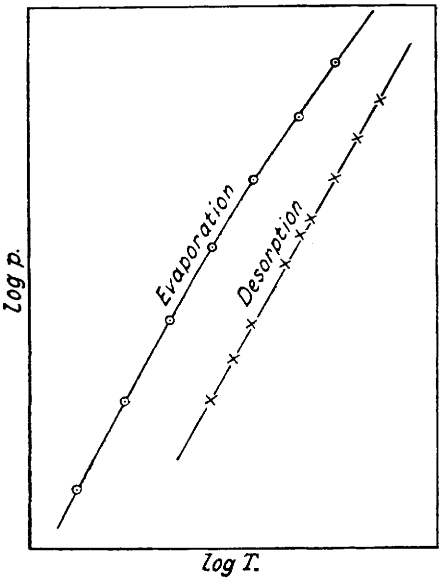
RESULTS.

The isosteric heat of adsorption, Q, was calculated from the equation, $d \log p/d(1/T) = -Q/2{\cdot}303\mathbf{R}$, which shows that the plot of log p against $1/T$ should be a straight line if Q is constant under the conditions of the experiments. Fig. 3 shows some of these plots for the various bases and the lines are satisfactorily straight. This means that the isosteric heat has no observable temperature coefficient. Brunauer (*op. cit.*, p. 262) calls attention to the fact that, if adsorption may be regarded as purely physical, the heat of adsorption should be practically temperature-independent.

The average values of $-Q$ for the bases pyridine, α-picoline, and diethylamine at different stages of adsorption are summarised in the Table. They are practically equal for all three compounds. It was not possible to measure $-Q$ for diethylamine at higher values of x/m owing to its larger equilibrium pressures. It is also seen that the heat values are not markedly different from those for the alcohols (methyl alcohol, 11470 at $x/m = 23{\cdot}97$; ethyl alcohol about 11500 for x/m varying from 87 to 40). The comparison is interesting when one considers the differences between the chemical properties of the two series of compounds and some of their physical properties, *e.g.*, dipole moments, 1·73—1·65 for methyl–butyl alcohol, 2·11 for pyridine. The net heat of adsorption (= isosteric heat of adsorption — latent heat of condensation of the vapour to a liquid in bulk) was again found to be positive throughout for pyridine and is probably so for the other bases (cf. *J. Indian Chem. Soc.*, *loc. cit.*). It amounts to about 18% of the isosteric heat under the conditions of these measurements.

FIG. 4.

Entropies of evaporation and desorption of pyridine on silica gel.



Heats of adsorption of bases on silica gel.

	x/m (10^{-4} g.-mol./ g. of gel).	$-Q$, cals./ g.-mol.		x/m (10^{-4} g.-mol./ g. of gel).	$-Q$, cals./ g.-mol.
Pyridine	71·5	11,270	α-Picoline	54·9	11,920
	66·0	11,850		53·1	11,020
	64·0	11,660	Diethylamine ...	22·1	12,010

Hildebrand (*J. Amer. Chem. Soc.*, 1915, **37**, 970) employs the equation $d \log p/d \log T = \Lambda/\mathbf{R}T$ to discuss the entropy changes accompanying evaporation of liquids. The quantity Λ has been called the entropy of evaporation; p is the vapour pressure of the liquid at the absolute temperature T. The quantity $\Lambda/\mathbf{R}$ which is proportional to the entropy may be obtained at any temperature T by plotting log p against log T, and measuring the slope of the resulting curve at the appropriate point. A similar procedure may be adopted with the data obtained in the present tensimetric measurements to see how far the entropy changes accompanying evaporation are analogous to those accompanying desorption. The upper curve of Fig. 4 refers to evaporation of liquid pyridine in bulk, the vapour-pressure data being those of Mann (*J. Amer. Chem. Soc.*, 1931, **53**, 453); the lower curve refers to the desorption of the same liquid from silica gel at constant amount of adsorption, 64 × 10^{-4} g.-mols. per g. of the gel. One notes that the entropy of evaporation falls off somewhat towards higher temperatures but that the entropy of desorption of the same liquid from silica gel, at a constant amount of adsorption is steady in the range of temperatures covered. However, the two curves have substantially equal slopes. This result may be interpreted to mean that the adsorbed molecules behave in a manner similar to, but not identical with, that in the ordinary liquid state with regard to the degrees of freedom.

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