39. *Adsorption by Oxide Gels from Liquid Mixtures containing Nitrogenous Bases.*

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Adsorption at 20° on alumina and on silica gel from liquid mixtures of pyridine, piperidine, or *n*-butylamine with a hydrocarbon involves two processes. Irreversible adsorption of the base occurs on a fraction of the surface, possibly owing to the formation of weak chemical bonds to the aluminium or silicon atoms, the strength of the bond being related to the basic strength of each adsorbate. Subsequent physical adsorption is competitive between the base and the hydrocarbon. The individual isotherms are obtained on the assumption that physical adsorption is unimolecular.

AT room temperature, slow chemisorption of the lower aliphatic alcohols by alumina, silica gel, and titania gel takes place provided that oxide ions occur at the surface. Measurements on vapour-phase adsorption showed that chemisorption proceeded until all accessible oxide ions had taken up alcohol.[1] Similar chemisorption occurs from liquid mixtures of the alcohol and an indifferent hydrocarbon such as benzene,[2] which may be of significance in chromatography.

As the chromatographic behaviour of nitrogenous bases is also of interest, we examined the adsorption of pyridine, piperidine, and *n*-butylamine severally from mixtures with either benzene or *cyclo*hexane. Each base was strongly adsorbed, so we could not analyse some of the isotherms of concentration change into reasonable individual isotherms by our usual method.[1] We therefore proceeded as for the alcohols to determine whether the bases were chemisorbed.[2] Some experiments were extended to ammonia, just as some of the work on alcohols was extended to water.

Vapour-phase Experiments.—The solids were saturated with the bases, and vapour-phase desorption was then carried out. The results (Table 1) show that significant irreversible adsorption takes place at 20°. In the cases examined the residual adsorption is less at 60° than at 20°. (The rate of desorption falls to zero in each case. The possibility that the low vapour pressure of the adsorbed bases might result in desorption's continuing at a very low rate seems most unlikely as a limit to desorption is also found with ammonia, which has a vapour pressure of some $8\frac{1}{2}$ atm. at 20°.) Chemisorption of the bases is completed more quickly than that of the alcohols; " irreversible adsorption " of the bases reaches a maximum within 24 hours' contact with the solid, whereas up to a week is required for the alcohols.

Isosteric heats of adsorption were also obtained from the 20° and 60° isotherms of adsorption of pyridine and of ammonia on boehmite. These are given in Table 2, where a comparison is made with the corresponding heats of adsorption of benzene and *cyclo*hexane which are undoubtedly held by physical forces only. The values for the bases

[1] Kipling and Peakall, *J.*, 1956, 4828.

[2] *Idem*, *J.*, 1957, 834, 4054.

are not only higher than those for the hydrocarbons, but also rise rapidly with fall in surface coverage, whereas the latter values rise very little. The contrast between the two pairs of adsorbates is further emphasised by evaluating the " net " heat of adsorption, $(E_x - E_L)$, *i.e.*, by subtracting from the total heat of adsorption (E_x) the latent heat of condensation of the vapour (E_L). The heats of adsorption of the bases are so high that at least part of the adsorption must be other than physical. In particular, the values of E_x for ammonia are higher than the maximum for physical adsorption given by Trapnell.[3] The values of $(E_x - E_L)$ thus obtained are considerably higher than those obtained from the term *c* of the BET equation. The values for benzene, however, agree well with those obtained calorimetrically by Gregg and Wheatley,[4] and those for the bases are close to Bastick's calorimetric values for adsorption of ammonia on silica gel.[5] It may thus be questioned whether the term *c* has its usual significance when mixed physical and chemical adsorption takes place.

TABLE 1. *Vapour-phase desorption of bases.*

Solid	Vapour	Time of contact (days)	Residual amount adsorbed (mmoles/g.)	Solid	Vapour	Time of contact (days)	Residual amount adsorbed (mmoles/g.)
Boehmite	Bu^nNH_2	1	0·52	" Gibbsite "	C_5H_5N	1	0·35
	$C_5H_{11}N$	1	0·65		C_5H_5N	1 *	0·16
	C_5H_5N	1	0·44				
	C_5H_5N	7	0·44	Silica gel-I	NH_3	3	1·54
	C_5H_5N	1 *	0·22		Bu^nNH_2	1	1·12
					$C_5H_{11}N$	1	1·38
γ-Al_2O_3-I	NH_3	3	0·76		C_5H_5N	1	0·96
	Bu^nNH_2	1	0·61		C_5H_5N	1 *	0·34
	$C_5H_{11}N$	1	0·73		C_5H_5N	7	0·95
	C_5H_5N	1	0·42				
	C_5H_5N	1 *	0·16	Silica gel-II	C_5H_5N	1	1·03

Desorption was continued until no further removal of adsorbate could be detected. The temperatures were 20° except for those marked * which were 60°.

TABLE 2. *Isosteric heats of adsorption on boehmite* (*kcal./mole adsorbed*).

Surface covered (%)	E_x	$E_x - E_L$	Surface covered (%)	E_x	$E_x - E_L$	Surface covered (%)	E_x	$E_x - E_L$	Surface covered (%)	E_x	$E_x - E_L$
Ammonia			Pyridine			Benzene			*cyclo*Hexane		
87	15·4	10·4	76	18·1	9·4	43	10·1	2·2	38	9·7	1·9
94	12·7	7·7	85	16·8	8·1	54	9·8	1·9	55	9·6	1·8
98	11·9	6·9	93	15·2	6·5	75	9·3	1·4	77	9·4	1·6
						97	9·2	1·3	89	9·3	1·5

Dobay, Fu, and Bartell [6] found similar high heats of adsorption for alkylamines on silica gel and concluded that adsorption in these systems could not be entirely physical. The strong adsorption of such bases by oxide gels may well be general, for Brown and Foster have shown that it occurs with ferric oxide gel.[7] They recorded desorption isotherms, but unfortunately not down to zero pressure, though this may indicate the difficulty of desorption compared with normal systems.

Liquid-phase Experiments.—In the liquid-phase experiments, the bases were adsorbed from mixtures with either benzene or *cyclo*hexane. Data are given in Fig. 1 and Tables 3—5 for the isotherms of concentration change. The vapour-phase experiments show

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[3] Trapnell, " Chemisorption," Butterworths, London, 1955.

[4] Gregg and Wheatley, " Proc. 2nd International Congress of Surface Chemistry," Butterworths, London 1957.

[5] Bastick, *Compt. rend.*, 1952, **234**, 1279.

[6] Dobay, Fu, and Bartell, *J. Amer. Chem. Soc.*, 1951, **73**, 308, cf. Dobay and Bartell, *ibid.*, 1950, **72**, 4388.

[7] Brown and Foster, *J.*, 1952, 1139.

what allowance must be made for irreversible adsorption, and the residual change in concentration can then be apportioned to the physical adsorption of the individual components. The resulting individual isotherms are given in Figs. 2 and 3 and Tables 6—8.

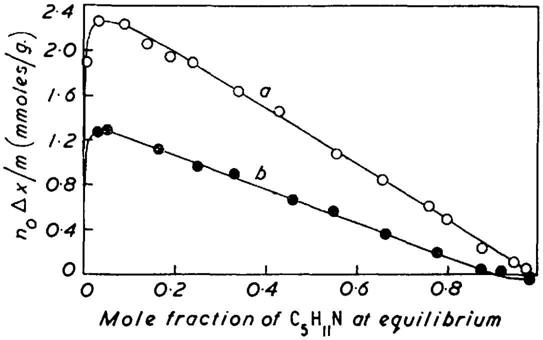

FIG. 1. *Isotherms of concentration change for adsorption at 20° from mixtures of piperidine and* cyclo*hexane on (a) silica gel and (b) boehmite.*

Δx is the decrease in mole fraction of the first-named component due to adsorption when n_0 mmoles of liquid are brought into contact with m g. of solid.

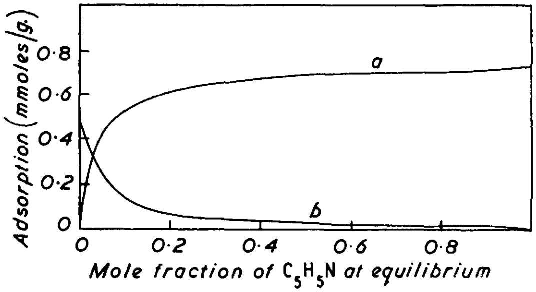

FIG. 2. *Physical adsorption (individual isotherms) by γ-Al_2O_3 at 20° from mixtures of (a) pyridine and (b)* cyclo*hexane.*

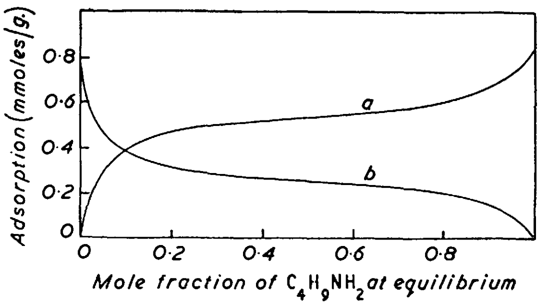

FIG. 3. *Physical adsorption (individual isotherms) by γ-Al_2O_3 at 20° from mixtures of (a)* n-*butylamine and (b) benzene.*

TABLE 3. *Adsorption from mixtures of pyridine and* cyclo*hexane; A, mole fraction of pyridine at equilibrium; B, $n_0\Delta x/m$ (mmoles/g.).*

A	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Boehmite, 20°		Silica gel, 20°		Boehmite, 60°		Silica gel, 60°		γ-Alumina, 20°	
0·03	1·41	0·02	2·64	0·07	1·20	0·01	1·83	0·04	0·80
0·07	1·44	0·06	3·07	0·17	1·19	0·05	2·70	0·10	0·84
0·14	1·38	0·11	3·19	0·26	1·06	0·09	2·90	0·18	0·83
0·29	1·16	0·15	3·14	0·32	0·94	0·14	2·76	0·29	0·74
0·37	1·02	0·24	2·95	0·40	0·84	0·19	2·78	0·38	0·63
0·48	0·82	0·33	2·65	0·48	0·71	0·30	2·51	0·50	0·56
0·59	0·66	0·45	2·22	0·60	0·53	0·37	2·24	0·59	0·46
0·69	0·46	0·55	1·84	0·65	0·49	0·40	2·06	0·68	0·36
0·77	0·35	0·66	1·40	0·71	0·34	0·45	2·00	0·76	0·24
0·83	0·21	0·72	1·05	0·80	0·20	0·52	1·62	0·83	0·19
0·89	0·12	0·78	0·89	0·93	0·04	0·63	1·32	0·92	0·09
0·94	0·06	0·86	0·48	0·97	0·02	0·68	1·06		
0·98	0·02	0·90	0·32			0·73	0·92		
						0·79	0·65		
						0·88	0·34		
						0·94	0·22		

TABLE 4. *Adsorption from mixtures of piperidine and* cyclo*hexane on γ-alumina at* 20°

Mole fraction of C_5H_{11} at equilibrium	0·02	0·06	0·11	0·16	0·20	0·25	0·36	0·49	0·57	0·67	0·81	0·88	0·95
$n_0\Delta x/m$ (mmoles/g.)	0·94	0·98	0·97	0·94	0·92	0·87	0·72	0·61	0·52	0·40	0·23	0·14	0·07

TABLE 5. *Adsorption from mixtures of* n-*butylamine and benzene; A, mole fraction of* Bu^nNH_2 *at equilibrium; B,* $n_0\Delta x/m$ *(mmoles/g.).*

A	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Boehmite, 20°		Boehmite, 20°		Silica gel, 20°		γ-Alumina, 20°	
0·01	0·90	0·60	0·55	0·01	2·61	0·03	0·76
0·03	1·05	0·67	0·45	0·05	2·73	0·07	0·86
0·09	1·09	0·70	0·41	0·11	2·82	0·13	0·85
0·11	1·07	0·80	0·19	0·15	2·78	0·19	0·82
0·20	1·04	0·91	0·06	0·26	2·43	0·29	0·65
0·21	1·03	0·92	−0·05	0·35	2·20	0·38	0·60
0·36	0·84	0·95	−0·07	0·44	1·90	0·47	0·51
0·47	0·72	0·97	−0·05	0·56	1·43	0·58	0·36
				0·68	1·02	0·69	0·19
				0·77	0·76	0·79	0·11
				0·89	0·44	0·90	−0·02
						0·96	−0·03

TABLE 6. *Physical adsorption (mmoles/g.) from mixtures of pyridine and* cyclo*hexane at* 20°.

Mole fraction of C_5H_5N at equilibrium	C_5H_5N	C_6H_{12}	C_5H_5N	C_6H_{12}
	on boehmite		on silica gel	
0·0	0·00	0·85	0·00	2·34
0·1	1·16	0·13	2·63	0·56
0·2	1·22	0·088	2·94	0·36
0·3	1·22	0·087	3·07	0·27
0·4	1·22	0·086	3·12	0·23
0·5	1·23	0·085	3·16	0·20
0·6	1·23	0·084	3·18	0·19
0·7	1·24	0·075	3·26	0·14
0·8	1·24	0·074	3·31	0·10
0·9	1·25	0·072	3·36	0·073
1·0	1·36	0·000	3·47	0·000

TABLE 7. *Physical adsorption (mmoles/g.) from mixtures of piperidine and* cyclo*hexane at* 20°.

Mole fraction of $C_5H_{11}N$ at equilibrium	$C_5H_{11}N$	C_6H_{12}	$C_5H_{11}N$	C_6H_{12}	$C_5H_{11}N$	C_6H_{12}
	on boehmite		on silica gel		on γ-Al_2O_3	
0·0	0·00	0·86	0·00	2·36	0·00	0·50
0·1	0·75	0·25	1·22	1·36	0·38	0·22
0·2	0·79	0·22	1·38	1·23	0·47	0·18
0·3	0·81	0·21	1·55	1·08	0·50	0·13
0·4	0·81	0·21	1·72	0·96	0·54	0·10
0·5	0·82	0·20	1·91	0·80	0·55	0·09
0·6	0·82	0·20	2·07	0·66	0·57	0·08
0·7	0·84	0·19	2·29	0·50	0·59	0·07
0·8	0·86	0·17	2·47	0·34	0·62	0·04
0·9	0·90	0·13	2·68	0·18	0·64	0·03
1·0	1·07	0·00	2·89	0·00	0·68	0·00

TABLE 8. *Physical adsorption (mmoles/g.) from mixtures of* n-*butylamine and benzene at* 20°

Mole fraction of Bu^nNH_2 at equilibrium	$BuNH_2$	C_6H_6	$BuNH_2$	C_6H_6
	on boehmite		on silica gel	
0·0	0·00	1·11	0·00	3·10
0·1	0·75	0·65	2·16	1·24
0·2	0·91	0·52	2·42	1·03
0·3	1·02	0·45	2·57	0·89
0·4	1·11	0·39	2·75	0·77
0·5	1·18	0·34	2·88	0·64
0·6	1·24	0·29	3·03	0·52
0·7	1·29	0·27	3·16	0·41
0·8	1·34	0·25	3·31	0·29
0·9	1·38	0·21	3·46	0·16
1·0	1·70	0·00	3·64	0·00

DISCUSSION

Irreversible Adsorption.—The irreversible adsorption of the bases might be attributed to salt-formation by the bases with residual acid left in the solids. The smaller extent of the irreversible adsorption at 60° than at 20° makes this unlikely to be a complete explanation. For the same reason, the irreversible adsorption we have observed is not comparable with the adsorption of nitrogenous bases on the " acid centres " of alumina-silica cracking catalysts; [8] such adsorption is observed at about 300°. It is more nearly comparable with that observed by Khodadadi,[9] who found that for temperatures below 20° the total adsorption of ammonia on silica gel was either independent of, or increased with rise in, temperature depending on the type of gel used.

Regarding the surface sites responsible for this weak irreversible adsorption, it has been suggested that ammonia is held to a glass surface by hydrogen-bonding, the O–H···N bond being more likely than N–H···O.[10] Hydrogen-bonding may well be an important factor in the physical adsorption shown by the systems we have studied, but it does not explain the whole of the irreversible adsorption. There is considerable irreversible adsorption of pyridine by γ-Al_2O_3, a combination which does not possess the hydrogen atoms required for hydrogen-bonding. This system, moreover, appears to be no different from the others recorded, as far as irreversible adsorption is concerned.

It seems significant that we find no critical difference in adsorption on anhydrous alumina, boehmite, and " gibbsite "; approximately the same proportion of each surface is covered irreversibly by a given adsorbate. The specific rôle of the oxide ions in chemisorption of alcohols [1,2] is thus not repeated here. Similarly the difference in the amounts of pyridine held by the original and the " dehydrated " silica gel (the latter having a reduced number of hydroxide groups) is not significant.

The remaining site for chemisorption is the aluminium or silicon atom. This would involve the formation of a co-ordinate bond from the nitrogen atom of the base. Pyridine forms such a bond with the aluminium atom in aluminium chloride,[11] and ammine complexes with iron are very stable.[12] A similar bond to the chromium ion is suggested to account for chemisorption of water by chromia at room temperature.[13] On this assumption, the maximum amounts of chemisorption possible on boehmite have been calculated, by use of molecular areas of 24·7 Å^2 for pyridine (calculated from data of Pauling and Schomaker [14]) and 12·8 Å^2 for ammonia (calculated from density data and tables of bond lengths and angles). The results (Table 9) are equivalent to 2·40 mmoles/g. for ammonia and 0·88 mmole/g. for pyridine, with an uncertainty similar to that discussed for chemisorption of alcohols.[1,2] The corresponding figures for γ-Al_2O_3 are 1·68 and 0·84 mmoles/g. respectively, which are much higher than those observed experimentally. Chemisorption clearly does not go to completion in this case. Together with the results for 60°, whereat

TABLE 9.

Plane	Area (Å^2)		No. of Al atoms		No. of Al atoms capable of reacting with			
					NH_3		C_5H_5N	
100	11·2	Total 39·1	1	Total 3	0·5	Total 2·0	0·25	Total 0·83
010	10·5		1		0·5		0·25	
001	17·4		1		1·0		0·33	

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[8] Mills, Boedeker, and Oblad, *J. Amer. Chem. Soc.*, 1950, **72**, 1554.

[9] Khodadadi, *Compt. rend.*, 1957, **244**, 198.

[10] Yates, Sheppard, and Angell, *J. Chem. Phys.*, 1955, **23**, 1980.

[11] Muller, *Z. anorg. Chem.*, 1931, **156**, 70.

[12] Sidgwick, " The Chemical Elements and their Compounds," Clarendon Press, Oxford, 1950, p. 1361.

[13] Voltz and Weller, *J. Amer. Chem. Soc.*, 1953, **75**, 5231.

[14] Pauling and Schomaker, *ibid.*, 1939, **61**, 1769.

irreversible adsorption still occurs but to a smaller extent, this shows that the bases are held by much weaker forces than those responsible for chemisorption of the alcohols.

The relative strengths of the co-ordinate bonds as indicated by the extent of chemisorption of the three bases on each adsorbent increase in the order of the basic dissociation constants (Table 10):

TABLE 10.

Irreversible adsorption (mmoles/g.) on:	Pyridine $K = 2{\cdot}3 \times 10^{-9}$	*n*-Butylamine $K = 4{\cdot}2 \times 10^{-4}$	Piperidine $K = 1{\cdot}6 \times 10^{-3}$
Boehmite	0·44	0·52	0·65
Silica gel	0·96	1·12	1·38
γ-Al_2O_3	0·42	0·61	0·73

Thus the extent of co-ordination to the aluminium or silicon atom increases as the extent of co-ordination to the proton increases. Ammonia is not included in this comparison because its smaller molecular size allows it access to a higher proportion of each surface than is available to the organic bases.

Adsorption from the Liquid Phase.—In adsorption from the liquid phase, the total process can be regarded as competitive physical adsorption, confined to one layer of physically adsorbed molecules, on a surface partially covered by irreversibly adsorbed base. The bases are physically adsorbed to a much greater extent than the indifferent hydrocarbons. The mole fraction of pyridine in the adsorbed phase on each adsorbent is greater than that of the other two bases, possibly partly because of its more polar character, but it may also be significant, as we observed elsewhere,[15] that the least volatile of otherwise similar substances is the most strongly adsorbed.

EXPERIMENTAL

Adsorbents.—The adsorbents were those described previously.[1, 2]

Adsorbates.—*n*-Butylamine was stored over sodium wire until evolution of hydrogen ceased, and fractionally distilled. It had n_D^{20} 1·4007 (cf. 1·4009 given by Vogel [16]). Piperidine was stored over solid potassium hydroxide and fractionally distilled. It had n_D^{20} 1·4528 (cf. 1·4533 given by Fowler [17]). Ammonia from a cylinder was dried by passing it over alumina and then over glass wool impregnated with sodium; the sodium was deposited by soaking the glass wool in a solution of sodium in liquid ammonia and evaporating off the ammonia. The purification of the other adsorbates has been described.[18]

Monolayer (BET) values for physical adsorption on the solids, following chemisorption of the respective base, are given in Figs. 2 and 3 and Tables 6—8, referred to 1 g. of the original solid.

Procedure.—Desorption experiments were carried out according to method A of our previous paper.[2] Liquid-phase adsorption was carried out at 20° by previous methods. As the " irreversible " adsorption was established rapidly for these systems, one day's contact only was allowed between adsorbent and adsorbate in the liquid-phase experiments. Table 11 shows that this procedure was satisfactory.

TABLE 11. *Adsorption on boehmite at 20° from a mixture of pyridine and* cyclo*hexane (equilibrium mole fraction of pyridine* = 0·215).

Time of shaking	1 hr.	2 hr.	4 hr.	8 hr.	1 day	3 days	7 days	14 days	27 days
$n_0\Delta x/m$ (mmoles/g.) *	1·18	1·23	1·28	1·26	1·27	1·27	1·27	1·27	1·26

* Mean of two values in each case.

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[15] Blackburn, Kipling, and Tester, *J.*, 1957, 2373.
[16] Vogel, *J.*, 1948, 1825.
[17] Fowler, *J. Appl. Chem.*, 1951, **1**, 848.
[18] Blackburn and Kipling, *J.*, 1954, 3819.