989. *Dipole Moments, and Sorption Characteristics at the Solution–Solid Interface of a Series of Substituted Azobenzenes.*

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Sorption of a series of substituted azobenzenes from benzene on activated alumina has been studied, and evidence provided that hydrogen-bond formation is responsible for the sorption process. From the isotherm data, standard thermodynamic free-energy changes have been calculated, and it is apparent that hydroxyazobenzenes have a greater affinity for the alumina surface than *p*-aminoazobenzene. Sorption saturation values are explained in terms of size and orientation of the sorbate molecules, and it is suggested that hydroxyazobenzenes may be sorbed on different surface sites from aminoazobenzenes. The apparent dipole moments of the azo-compounds in benzene and dioxan have been determined from measurements on dilute solutions, but no correlation between $\Delta\mu$ and free-energy decrease on sorption is observed. That the dipole moments of 2-hydroxy-5-methylazobenzene in benzene and dioxan are almost the same is considered to be evidence of intramolecular hydrogen bonding in this compound. Dipole moments of the azo-compounds in benzene are compared with those of the corresponding benzene derivatives, and explained by the difference in the $+M$ effect of the amino- and the hydroxy-group.

This investigation was carried out to determine if thermodynamic free-energy decrease on sorption at the solution–solid interface is reflected in the dipole moments of the sorbates.

Sorption of a series of substituted azobenzenes from benzene on activated alumina has been studied, and standard free-energy decreases associated with the sorption process have been evaluated. Dipole moments of the sorbates in benzene and dioxan have also been determined.

Of the sorbates used, the monosubstituted compounds are of interest in that they have been used [1,2] in determining an arbitrary gradation of activities of chromatographic alumina. It was expected that these compounds would exhibit wide variation of polarity and sorptive affinity for alumina. Benzene was chosen as solvent for the sorption study because of its non-polar character. In the light of Kiselev's work,[3] however, it appears that, although non-polar, benzene does not show the lowest interactions with oxide surfaces. For example, the sorption and heat of sorption of benzene on hydrated silica are higher than those of hexane, owing to additional interactions with the acid hydroxyl groups of the sorbent surface.

Experimental

(1) *Sorption Studies.*—(a) *Materials.* Chromatographic alumina, passing a 120-mesh B.S. sieve, was stored in bulk; 2·0 g. portions were dried at 110° for 48 hr. before use in the sorption experiments. Preliminary experiments indicated that drying of the alumina to constant

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[1] Brockmann and Schodder, *Ber.*, 1941, **74**, 73.

[2] Brockmann, *Discuss. Faraday Soc.*, 1949, **7**, 58.

[3] Kiselev, 2nd Internat. Congress of Surface Activity, "Solid/Gas Interface," Butterworths Scientific Publ., London, 1957, p. 179.

weight was complete after 48 hr. at 110°, and resulted in a 1·5% loss in weight, due presumably to removal of adsorbed moisture.

Benzene, dried over sodium wire, was distilled, and the fraction of b. p. 80·1°/760 mm. was collected.

p-Aminoazobenzene, recrystallised from alcohol, had m. p. 124°. *p*-Hydroxyazobenzene, prepared in the normal manner, was recrystallised from acetic acid and then alcohol, and had m. p. 153°. *p*-Methoxyazobenzene, prepared by treating *p*-hydroxyazobenzene with dimethyl sulphate in alkaline solution at 60°, was recrystallised from acetic acid and then alcohol, and had m. p. 55°. *p*-Acetamidoazobenzene, m. p. 146°, and *p*-acetoxyazobenzene, m. p. 88°, prepared by acetylation, were recrystallised from alcohol. *p*-Dimethylaminoazobenzene, prepared by coupling diazotised aniline with dimethylaniline in acid solution, was recrystallised from alcohol and had m. p. 118°. 4-Hydroxy-3-methyl-, m. p. 129°, 4-hydroxy-2-methyl-, m. p. 105°, and 2-hydroxy-5-methyl-azobenzene, m. p. 108°, were prepared by the normal coupling process and recrystallised from alcohol.

(b) *Method of sorption.* The sorption experiments were carried out at 35° as previously described[4] except that equilibrium concentrations were determined on a Hilger Spekker photoelectric absorptiometer.

(c) *Sorption results.* For the sorption process, free sorbate molecules + vacant sites $\rightleftharpoons$ occupied sites, if all sites are identical and there is no sorbate interaction, then $K = \theta/(1 - \theta)c$, it being assumed that the activity coefficients of the occupied and unoccupied sites are the same. θ is the fraction of surface covered, c is the concentration of the free sorbate molecules in the mobile phase (in mole l.^{-1}), an activity coefficient of unity being assumed, and K is an equilibrium constant for sorption. This equation can be rewritten in the form $\theta = Kc/(1 + Kc)$, which

TABLE 1. *Sorption and free-energy data.*

p-Hydroxyazobenzene

$10^4x_1 = 2{\cdot}97$; $10^{-4}K = 0{\cdot}64$; $-\Delta G^\circ = 5400$ cal. mole^{-1}.

10^4c	2·03	7·66	18·23	35·06	49·89
10^4x_0	1·840	2·330	2·695	2·895	3·145

4-Hydroxy-3-methylazobenzene

$10^4x_1 = 2{\cdot}12$; $10^{-4}K = 0{\cdot}49$; $-\Delta G^\circ = 5200$ cal. mole^{-1}.

10^4c	5·94	6·60	8·30	10·30	14·15	16·98
10^4x_0	1·435	1·532	1·691	1·775	1·855	1·885

4-Hydroxy-2-methylazobenzene

$10^4x_1 = 2{\cdot}21$; $10^{-4}K = 2{\cdot}51$; $-\Delta G^\circ = 6200$ cal. mole^{-1}.

10^4c	0·98	1·22	1·70	2·31	3·30	4·31
10^4x_0	1·530	1·650	1·730	1·820	1·930	2·009

2-Hydroxy-5-methylazobenzene

$10^4x_1 = 0{\cdot}41$; $10^{-4}K = 2{\cdot}28$; $-\Delta G^\circ = 6100$ cal. mole^{-1}.

10^4c	0·24	0·38	0·60	0·91	1·33	2·39	3·42
10^4x_0	0·118	0·165	0·221	0·283	0·323	0·353	0·361

p-Acetoxyazobenzene

$10^4x_1 = 1{\cdot}66$; $10^{-4}K = 1{\cdot}51$; $-\Delta G^\circ = 5900$ cal. mole^{-1}.

10^4c	1·31	3·00	4·63	10·00	18·52	37·86
10^4x_0	1·218	1·375	1·447	1·550	1·608	1·636

p-Aminoazobenzene

$10^4x_1 = 0{\cdot}67$; $10^{-4}K = 0{\cdot}06$; $-\Delta G^\circ = 3900$ cal. mole^{-1}.

10^4c	5·15	13·27	17·00	20·00	23·81	30·00	36·37	50·85
10^4x_0	0·123	0·296	0·345	0·375	0·408	0·444	0·469	0·480

p-Acetamidoazobenzene

$10^4x_1 = 0{\cdot}61$; $10^{-4}K = 0{\cdot}58$; $-\Delta G^\circ = 5300$ cal. mole^{-1}.

10^4c	2·12	5·00	8·50	15·09	26·79	38·79
10^4x_0	0·261	0·405	0·495	0·560	0·575	0·584

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[4] Erić, Goode, and Ibbitson, *J.*, 1960, 55.

is the familiar Langmuir isotherm. On replacement of θ by x_0/x_1, where x_0 = moles of solute sorbed per g. of alumina at equilibrium, and x_1 = moles sorbed at saturation, the Langmuir equation is transposed to give $c/x_0 = 1/x_1K + c/x_1$. This equation was found to be applicable to the sorption data in Table 1, and by measurement of the slopes and intercepts of the plots of c/x_0 against c, x_1, and K were calculated for each sorbate. The standard free-energy of sorption, $-\Delta G^0$, was calculated from equation $-\Delta G^0 = \boldsymbol{R}T \ln K$, this quantity providing a measure of the strength of the sorption bond. Sorption and free-energy data are presented in Table 1.

(2) *Dipole Moments.*—(a) *Materials.* Dioxan was repeatedly refluxed with sodium, and then fractionally distilled under anhydrous conditions.

(b) *Apparatus and methods.* Dielectric constants and refractive indices of solutions of graded concentrations of each sorbate in benzene and dioxan were determined at 25·0°. The apparatus and methods used were the same as in a previous investigation,[4] and the results are summarised in Table 2, where the symbols have their usual significance.

TABLE 2.

$100w$	ε	$n_{\rm D}$	$100w$	ε	$n_{\rm D}$	$100w$	ε	$n_{\rm D}$	$100w$	ε	$n_{\rm D}$
p-Aminoazobenzene in benzene			*p*-Aminoazobenzene in dioxan			*p*-Hydroxyazobenzene in benzene			*p*-Hydroxyazobenzene in dioxan		
0·000	2·2725	1·4981	0·000	2·2063	1·4200	0·000	2·2725	1·4981	0·000	2·2138	1·4201
0·118	2·2776	1·4985	0·096	2·2132	1·4202	0·093	2·2742	1·4982	0·198	2·2209	1·4206
0·227	2·2821	1·4988	0·190	2·2198	1·4206	0·181	2·2764	1·4984	0·292	2·2241	—
0·342	2·2871	1·4992	0·286	2·2267	1·4209	0·270	2·2782	1·4986	0·393	2·2276	1·4211
0·447	2·2916	1·4995	0·382	2·2329	—	0·361	2·2799	1·4987	0·584	2·2343	1·4218
0·556	2·2963	1·4999	0·478	2·2391	1·4218	0·452	2·2820	1·4989	0·770	2·2414	1·4222
4-Hydroxy-3-methylazobenzene in benzene			4-Hydroxy-3-methylazobenzene in dioxan			4-Hydroxy-2-methylazobenzene in benzene			4-Hydroxy-2-methylazobenzene in dioxan		
0·000	2·2725	1·4981	0·000	2·2115	1·4200	0·000	2·2725	1·4981	0·000	2·2128	1·4200
0·227	2·2767	1·4986	0·192	—	1·4206	0·215	2·2768	1·4985	0·195	2·2188	1·4206
0·451	2·2807	1·4991	0·382	2·2255	1·4213	0·444	2·2815	1·4988	0·392	2·2249	1·4213
0·676	2·2850	1·4995	0·579	2·2325	1·4220	0·547	2·2838	1·4991	0·507	2·2285	1·4217
0·898	2·2893	1·5000	0·767	2·2398	1·4226	0·658	2·2858	1·4993	0·605	2·2316	1·4220
1·128	2·2937	1·5005	0·960	2·2460	1·4232	0·872	2·2900	1·4996	0·790	2·2373	1·4226
2-Hydroxy-5-methylazobenzene in benzene			2-Hydroxy-5-methylazobenzene in dioxan			*p*-Methoxyazobenzene in benzene			*p*-Methoxyazobenzene in dioxan		
0·000	2·2725	1·4981	0·000	2·2133	1·4200	0·000	2·2725	1·4981	0·000	2·2091	1·4200
0·216	2·2755	1·4985	0·182	2·2165	1·4205	0·092	2·2742	1·4982	0·194	2·2129	1·4202
0·440	2·2786	1·4989	0·374	2·2195	1·4210	0·181	2·2758	1·4984	0·384	2·2167	1·4206
0·663	2·2817	1·4993	0·567	2·2228	1·4215	0·272	2·2776	1·4986	0·482	2·2186	1·4207
0·886	2·2846	1·4997	0·760	2·2263	1·4219	0·361	2·2790	1·4987	0·577	2·2204	1·4209
						0·452	2·2808	1·4989	0·769	2·2242	1·4213
p-Dimethylaminoazobenzene in benzene			*p*-Acetamidoazobenzene in benzene			*p*-Acetoxyazobenzene in benzene					
0·000	2·2725	1·4981	0·000	2·2725	1·4981	0·000	2·2725	1·4981			
0·115	2·2790	1·4983	0·114	2·2814	1·4982	0·123	2·2744	1·4982			
0·230	2·2859	1·4986	0·183	2·2865	1·4984	0·225	2·2760	1·4983			
0·345	2·2922	1·4989	0·224	2·2898	—	0·340	2·2778	1·4985			
0·453	2·2978	1·4992	0·226	2·2901	1·4985	0·453	2·2796	1·4986			
0·562	2·3041	1·4994	0·340	2·2990	1·4987	0·566	2·2815	1·4987			

The molar orientation polarisation at infinite dilution, $P_{2\infty}$, and the dipole moment, μ, of each azobenzene derivative were calculated from equations (1) and (2) respectively,

$$P_{2\infty} = 3M_2v_1\{\alpha/(\varepsilon_1 + 2)^2 - \nu/(n_1{}^2 + 2)^2\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\mu = 0{\cdot}012812\,(P_{2\infty} \times T)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

M_2 = molecular weight of solute; v_1, ε_1, and n_1 are specific volume, dielectric constant, and refractive index respectively of the solvent at 25·0°; $\alpha = (d\varepsilon/dw)_{w=0}$, $\nu = (dn^2/dw)_{w=0}$. α and ν were determined from the limiting slopes of the plots of ε against w, and $n^2{}_{\rm D}$ against w.

DISCUSSION

Polarisation and sorption data are summarised in Table 3.

In the present work, although alumina was slightly coloured after standing in contact with solutions of azobenzene in benzene, the extent of sorption was not measurable.[5] This confirms that the main source of affinity between the sorbates used and the alumina surface is in the polar substituent groups. Evidence that hydrogen bonding is primarily responsible for sorption of non-ionic solutes on alumina is available from a number of sources.[6,7] *p*-Methoxyazobenzene and *p*-dimethylaminoazobenzene are not sorbed by the alumina used in this investigation, and it is evident from the data in Table 3 that, with the exception of *p*-acetoxyazobenzene, only those compounds containing substituent groups capable of hydrogen bonding with the sorbent surface are sorbed with a measurable free-energy decrease. From a study of the influence of proton-accepting solutes on the surface film properties of cetyl acetate, Allingham, Giles, and Neustädter [8] obtained evidence of intermolecular hydrogen bonding, the acetate group acting as proton donor. These authors suggest that hydrogen bonding occurs through a hydrogen atom of the methyl residue in the acetyl group which is activated by the adjacent carbonyl-oxygen atom. A similar mechanism may operate in the sorption of *p*-acetoxyazobenzene on alumina, the sorbate acting as proton donor. Alternatively, the acetyl group may act as the acceptor group in hydrogen bonding, with the alumina surface as proton donor.

TABLE 3. *Polarisation and sorption data.*

Azobenzene deriv.	Solv.*	$10^3\alpha$	$10^2\nu$	$P_{2\infty}$ (c.c.)	μ (D)	$-\Delta G^\circ$ (cal. mole^{-1})	10^4x_1	Previous * values of μ (D)
p-Amino-	B	4246	98	120·3	2·43	3900	0·67	B 15·4° 2·71,[a]
	D	6920	102	188·8	3·04			B 2·48 [b]
p-Hydroxy-	B	2090	56	56·7	1·66	5400	2·97	B 14·7° 1·62,[a]
	D	3557	78	87·9	2·07			D 15·2° 2·04 [a]
4-Hydroxy-3-methyl-	B	1882	64	49·0	1·55	5200	2·12	
	D	3631	93	91·1	2·11			
4-Hydroxy-2-methyl-	B	2022	55	58·4	1·69	6200	2·21	
	D	3094	92	72·3	1·88			
2-Hydroxy-5-methyl-	B	1347	54	32·1	1·25	6100	0·41	
	D	1702	73	31·2	1·23			
p-Methoxy-	B	1877	58	51·3	1·58	—	—	B 22·8° 1·29 [a]
	D	1965	49	49·4	1·55			
p-Dimethylamino-	B	5602	71	206·8	3·18	—	—	B 26·9° 3·68,[a] B 25° 3·22 [11]
p-Acetamido-	B	7826	57	326·2	3·99	5300	0·61	
p-Acetoxy-	B	1568	36	54·3	1·63	5900	1·66	

* B = benzene; D = dioxan.

[a] Bergmann and Weizmann, *Trans. Faraday Soc.*, 1936, **32**, 1318. [b] Campbell, McAllister, and Rogers, *J. Amer. Chem. Soc.*, 1953, **75**, 864. Other refs. as in text.

The affinity of *p*-hydroxyazobenzene for the alumina surface is appreciably greater than that of *p*-aminoazobenzene, indicating that the hydroxyl group forms stronger bonds than the amino-group. Although it is rather surprising that $-\Delta G^0$ for *p*-acetoxyazobenzene is greater than that for *p*-hydroxyazobenzene, the result is consistent with the high $-\Delta G^0$ value for *p*-acetamidoazobenzene in comparison with the value for *p*-aminoazobenzene, *i.e.*, replacement of a hydrogen atom of a hydroxy- or amino-group by the acetyl group causes an increase in $-\Delta G^0$.

Of the disubstituted azobenzenes examined, it is noteworthy that the dipole moment of 2-hydroxy-5-methylazobenzene is almost the same in benzene as in dioxan, indicating the presence of intramolecular hydrogen bonding in this compound. Hoyer [7] concludes

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[5] Jackson, M.Sc. Thesis, Leeds, 1958.

[6] Cummings, Garren, Giles, Rahman, Sneddon, and Stewart, *J.*, 1959, 535; Giles, Mehta, Stewart, and Subramanian, *J.*, 1954, 4360.

[7] Hoyer, *Kolloid-Z.*, 1951, **121**, 121.

[8] Allingham, Giles, and Neustädter, *Discuss. Faraday Soc.*, 1954, **16**, 92.

that the sorption of simple non-ionic anthraquinones and azo-compounds on alumina columns (judged by speed of travel) is weaker when any amino-, hydroxy-, etc., groups they contain are internally chelated, than when they are free. The relatively high value of $-\Delta G^0$ (6100 cal. mole^{-1}) for 2-hydroxy-5-methylazobenzene does not appear to confirm this conclusion.

The previously determined x_1 value for phenol ($4{\cdot}59 \times 10^{-4}$) indicates almost complete unimolecular coverage of the alumina surface.[4] Increased cross-sectional area of the azobenzene molecule, and surface-area requirements of the acetoxy- and methyl groups are suggested as factors responsible for the smaller x_1 values of *p*-hydroxyazobenzene and its derivatives. Sorption of 2-hydroxy-5-methylazobenzene through the hydroxyl group in the 2-position would produce a tilted arrangement of molecules on the sorbent surface, and the consequently increased surface-area requirements of the sorbed molecules may explain the very small x_1 value of this compound.

A marked difference exists between the sorption saturation values of the hydroxy- and amino-azobenzenes, and two explanations appear possible. First, it could be argued that both types of compound are sorbed by the same sites, the hydroxyl group forming stronger bonds with the sorbent surface than the amino-group. Since the availability of suitable sites, and the dimensions of the sorbate molecules, also determine the extent of surface saturation, and since the surface requirements of the hydroxy- and amino-groups are not very different, it is possible that the two types of compound are sorbed on different surface sites. Unfortunately, no evidence is available that the alumina surface is, in fact, heterogeneous.

Table **3** indicates that the dipole moment of the sorbate determined in either benzene or dioxan is unrelated to free-energy decrease on sorption. In agreement with other workers,[9] it is found that in the case of those compounds capable of hydrogen bonding through the hydrogen atom of the hydroxy- or amino-group and the oxygen atom of the dioxan molecule, the dipole moments determined in dioxan are all greater than those in benzene. It was expected that $\Delta\mu(\mu_D - \mu_B)$ would be parallel with free-energy changes on sorption, but such is not the case, and it seems more likely that variations in the magnitude of the O–H or N–H bond moment on sorption may be significant in interpreting variations in sorption affinity. This appears to be so from a study of dipole moments, and sorption affinity for alumina, of a series of substituted phenols.[4]

The dipole moments of the compounds studied are of interest. A comparison of the data in Table 4 shows that the moments of the hydroxyazobenzenes do not differ greatly from those of the corresponding benzene derivatives, indicating the absence of *cis*-isomers in the former compounds (dipole moments of *cis*- and *trans*-azobenzene are **3·0** D and zero, respectively[10]). Also the increased length of the conjugated system in the hydroxyazobenzenes would appear to have very little effect on the mesomeric electron release of the hydroxyl group. Campbell, Young, and Rogers[11] suggest, however, that it is just this

TABLE 4.

Substituent	4-OH	4-OMe	4-OAc	4-OH, 3-Me	4-OH, 2-Me
μ (D) (azobenzene deriv.) ...	1·66	1·58	1·63	1·55	1·69
μ (D) (benzene deriv.)	1·54 [a]	1·30 [b]	1·52 [c]	1·44 [d]	1·60 [d]
Substituent	2-OH, 5-Me	4-NH$_2$	4-NMe$_2$	4-NHAc	
μ (D) (azobenzene deriv.) ...	1·25	2·43	3·18	3·99	
μ (D) (benzene deriv.)	1·57 [a]	1·51 [9b]	1·58 [9b]	4·01 [e]	

[a] Goode and Ibbitson, *J.*, 1960, 4265. [b] Le Fèvre, "Dipole Moments," Methuen, London, 1953, p. 134. [c] Donle, *Z. phys. Chem.*, 1931, **14**, *B*, 326. [d] Williams, *Phys. Z.*, 1928, **29**, 683. [e] Le Fèvre and Le Fèvre, *J.*, 1936, 1130.

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[9] (*a*) Vassiliev and Syrkin, *Acta Physicochim. U.R.S.S.*, 1941, **14**, 414; (*b*) Few and Smith, *J.*, 1949, 753; (*c*) *idem, ibid.*, p. 2663; (*d*) Smith, *J.*, 1950, 3532; (*e*) *idem, J.*, 1953, 109; (*f*) Smith and Walshaw, *J.*, 1957, 3217.

[10] Hartley and Le Fèvre, *J.*, 1939, 531.

[11] Campbell, Young, and Rogers, *J. Amer. Chem. Soc.*, 1951, **73**, 5789.

type of electron interaction which accounts for the increased dipole moments of *p*-amino- and *p*-dimethylamino-azobenzene as compared with aniline and dimethylaniline respectively. The greater difference found for the dimethylamino-group (1·60 D) may be due to electron release from the two methyl groups attached to the nitrogen atom and hence to the conjugated system. Interaction on a smaller scale would be expected in the case of hydroxyl and methoxyl groups in view of the sequence $NH_2 > OMe > OH$ for the mesomeric electron release from these groups ($+M$ effect). The dipole moments of *p*-acetamidoazobenzene and acetanilide are almost identical, indicating that the acetyl group decreases the mesomeric interaction between the nitrogen *p*-electrons and the azo-link or distant benzene ring.

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