

## LINEAR ELUTION ADSORPTION CHROMATOGRAPHY

## XII. FUNCTIONAL GROUP ADSORPTION ENERGIES ON THE METAL OXIDE ADSORBENTS

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## INTRODUCTION

Solute adsorption energies  $S^\circ$  determine the retention volumes and separation order of sample components in linear elution adsorption chromatography (LEAC) (e.g. Part XI<sup>1</sup>). These solute adsorption energies are in turn defined by the adsorption energies  $Q^\circ_i$  of individual solute groups or substituents, although the interactions between different groups in the same molecule must also be taken into account<sup>1</sup>. The adsorption energies of different groups in the *eluent* molecule also determine its strength  $\varepsilon^\circ$  (ref. 2). The first tabulation of relative adsorption strengths (on alumina) of different functional groups was that of BROCKMANN<sup>3</sup>. Numerous quantitative data for functional group adsorption energies have since been reported for alumina, Florisil, and silica<sup>4-10</sup>.  $Q^\circ_i$  values for a given group  $i$  (e.g. bromo, nitro, amino) are considered to vary with the adsorbent type (e.g. alumina *versus* silica) and with whether  $i$  is attached to aliphatic or aromatic substituents, or to both. If relationships between  $Q^\circ_i$  values for different adsorbents, and for aliphatic *versus* aromatic substituents could be established, it would greatly reduce the data required for prediction of separation in different chromatographic systems. It would also simplify the classification of the fundamental differences in the separation capabilities of different adsorbents. Finally it would further clarify the fundamental molecular processes which determine solute adsorption energies. The present paper will show the existence of such relationships and discuss some of their implications.

## EXPERIMENTAL

Retention volume data for elution from alumina (Alcoa, F-20) and silica (Davison code 12) were obtained as previously (e.g. refs. 5, 7), in order to supplement previous  $Q^\circ_i$  values for these two adsorbents. The linear equivalent retention volume  $\bar{R}^\circ$  for pentane elution of benzothiophene from 7.5%  $H_2O-SiO_2$  (Davison code 12) was 6.1 ml/g, compared to a value of 6.3 for naphthalene. From this it was calculated that  $S^\circ$  for the adsorption of benzothiophene on silica is 2.00, and  $Q^\circ_i$  for the sulfur group is therefore about 0.02 less than  $Q^\circ_i$  for two aromatic carbons, or  $Q^\circ_i$  (—S—) equals 0.48 in benzothiophene. Log  $\bar{R}^\circ$  for elution of N-methylcarbazole from 22%

H<sub>2</sub>O-SiO<sub>2</sub> by pentane was equal 0.48, from which  $S^\circ$  was calculated equal 3.30, and  $Q_i^\circ$  equal 0.96 for the —N(CH<sub>3</sub>)— group in this molecule.

The following data were obtained for elution from 3.8 % H<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub> (Alcoa F-20). Log  $\underline{R}^\circ$  for elution of benzal-methylamine by methylene chloride was —0.17.  $S^\circ$  for this solute was calculated equal 6.3. Benzanilide eluted by 52 % v methylene chloride-pentane and by methylene chloride gave log  $\underline{R}^\circ$  values equal 0.97 and 0.18, respectively. From these values  $S^\circ$  was calculated equal 8.59. Pentane elution of *n*-butanethiol and diethyl disulfide gave log  $\underline{R}^\circ$  values equal 0.04 and —0.04, respectively.  $S^\circ$  values for these two solutes were then calculated, equal 2.86 and 2.74, respectively. Log  $\underline{R}^\circ$  for benzoic acid eluted by 35 % v isopropanol-pentane was larger than 2.00, from which  $S^\circ$  was calculated as greater than 12.4.

## DISCUSSION

### *Aliphatic versus aromatic substituents*

Previous studies<sup>4,8</sup> have established that  $Q_i^\circ$  for a group *i* adsorbed on a given adsorbent varies widely, depending on whether *i* is substituted on a saturated hydrocarbon chain (*e.g.* R—S—R,  $Q_s^\circ$  equal 2.65 on alumina), on an aromatic ring (*e.g.*  $\phi$ —S—R,  $Q_s^\circ$  equal 1.32), or is part of an aromatic ring (*e.g.* thiophene,  $Q_s^\circ$  equal 0.76). Various explanations have been offered for these differences in  $Q_i^\circ$  values<sup>4,5</sup>. Thus substituents which possess unsaturation or *p*-electrons can conjugate with the aromatic ring, which in turn should affect the availability of these electrons for interaction with adsorption sites. Similarly an aromatic substituent on a group *i* (*i.e.* phenyl) should sterically interfere with the adsorption of *i* to a greater extent than an alkyl group such as methyl. Both of these explanations predict a lessening of  $Q_i^\circ$  when an aliphatic substituent is replaced by an aromatic substituent. In support of these theories it is generally noted that  $Q_i^\circ$  is substantially lower for aromatic groups *i* than for aliphatic groups. Two additional factors determine the apparent difference between aromatic and aliphatic group  $Q_i^\circ$  values; ring delocalization<sup>2</sup> and ring electronic activation<sup>1,6</sup>, when an aromatic ring is attached to *i*. Strongly adsorbing groups *i* tend to reduce the adsorption energies of attached aromatic rings by delocalization of the ring, and electron withdrawing groups reduce the adsorption energy of attached rings. Neither effect can significantly influence the adsorption energies of attached aliphatic groups, since these are very weakly adsorbed. Since ring delocalization and electronic activation are normally ignored in calculating aromatic  $Q_i^\circ$  values, this effect is incorporated in the resulting ("nominal")  $Q_i^\circ$  values.

Table I summarizes a number of  $Q_i^\circ$  values for groups with both aliphatic and aromatic substituents. These data permit a detailed examination of the reasons for differences in  $Q_i^\circ$  values between aromatic and aliphatic groups. Three classes of groups *i* may be distinguished: (I) groups with no "normal" double bonds (the semi-polar bonds of the nitro group are not considered normal double bonds); (II) groups with ordinary double bonds; (III) hydrogen bonding groups (*e.g.* —OH). Table I includes all available data where both aliphatic and aromatic  $Q_i^\circ$  values have been measured for the same group *i*, exclusive of basic groups on silica and acidic groups on alumina. These latter values are excluded because of preferential adsorption of acids on alumina and bases on silica (see following section). The aromatic  $Q_i^\circ$  values can be corrected for ring delocalization and electronic activation as described previously<sup>1,2</sup>. Fig. 1 shows

TABLE I

CORRELATION OF  $Q^{\circ}_i$  VALUES FOR ALIPHATIC AND AROMATIC FUNCTIONAL GROUPS

Group	Adsorbent	Ref.*	$Q^{\circ}_i$		Ring	Ring	Net $Q^{\circ}_i$ (arom.) <sup>§</sup>	$Q^{\circ}_i$ (aliph.) minus net $Q^{\circ}_i$ (arom.)
			Aliph.	Arom.	deloc.** $\Delta_L$	activ.**.* $\Delta\sigma$		
<i>Class I</i>								
—Cl	Al <sub>2</sub> O <sub>3</sub>	a, b	1.82	0.20	0.00	0.17	0.37	1.45
—Br	Al <sub>2</sub> O <sub>3</sub>	a, c	2.00	0.33	0.00	0.18	0.51	1.49
—I	Al <sub>2</sub> O <sub>3</sub>	a, c	2.00	0.51	0.00	0.18	0.69	1.31
—S—R	Al <sub>2</sub> O <sub>3</sub>	c	2.65	1.32	0.20	0.02	1.54	1.11
—O—R	Al <sub>2</sub> O <sub>3</sub>	c	3.50	1.77	0.39	—0.03	2.13	1.37
—NO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	c, d	5.40	2.77	0.75	0.25	3.77	1.63
Average								1.39 ± 0.17 (S.D.)
—Cl	SiO <sub>2</sub>	e, f	1.32	—0.20	0.00	0.14	—0.06	1.38
—Br	SiO <sub>2</sub>	e, f	1.32	—0.17	0.00	0.14	—0.03	1.35
—I	SiO <sub>2</sub>	e, f	1.20	—0.15	0.00	0.14	—0.01	1.21
—S—R	SiO <sub>2</sub>	e, f	2.94	1.29	0.15	0.02	1.46	1.48
Average								1.36 ± 0.11 (S.D.)
<i>Class II</i>								
—O <sub>2</sub> C—R	Al <sub>2</sub> O <sub>3</sub>	c	5.00	3.48	0.94	0.20	4.62	0.38
—CO—R	Al <sub>2</sub> O <sub>3</sub>	c	5.00	3.74	1.00	0.11	4.85	0.15
—CO <sub>2</sub> —R	Al <sub>2</sub> O <sub>3</sub>	c	5.00	3.32	0.92	0.13	4.37	0.63
—C≡N	Al <sub>2</sub> O <sub>3</sub>	c	5.00	3.25	0.89	0.25	4.39	0.61
—CO <sub>2</sub> — $\phi$	Al <sub>2</sub> O <sub>3</sub>	c	5.18	4.02	0.84	0.15	5.01	0.17
—CO— $\phi$	Al <sub>2</sub> O <sub>3</sub>	c, g	5.60	4.36	0.92	0.11	5.39	0.21
—N=C— $\phi$	Al <sub>2</sub> O <sub>3</sub>	h, i	6.30	4.14	0.95	~ 0.14	5.23	1.07
—CO—NH— $\phi$	Al <sub>2</sub> O <sub>3</sub>	h, i	8.20	7.04	1.27	0.08	9.39	—0.19
Average								0.38 ± 0.38 (S.D.)
<i>Class III</i>								
—OH	SiO <sub>2</sub>	j	5.60	4.20	0.85	—0.04	5.01	0.59
Average								0.59

\* (a) ref. 5; (b) unreported data; *n*-C<sub>10</sub>—Cl gave  $Q^{\circ}_i$  equal 1.82 for —Cl on 0.7% H<sub>2</sub>O—Al<sub>2</sub>O<sub>3</sub>; (c) ref. 6; (d) ref. 2; (e) ref. 1; (f) unreported data, see Part XIII; (g) ref. 9; (h) ref. 10; (i) experimental section; (j) ref. 4 (see ref. 7).

\*\* From Fig. 1.

\*\*\*  $\Delta\sigma = 0.31(1.86 - \Delta_L)\bar{\sigma}$  for Al<sub>2</sub>O<sub>3</sub>;  $\Delta\sigma = 0.31(1.50 - \Delta_L)\bar{\sigma}$  for SiO<sub>2</sub>; values of  $\bar{\sigma}$  from JAFFER<sup>12</sup>.

§ Equation 1.

the ring delocalization energy  $\Delta_L$  versus the nominal  $Q^{\circ}_i$  value of the aromatic substituent (the latter is calculated from  $S^{\circ}$  for the *i*-substituted benzene, assuming no delocalization or electronic activation of the aromatic ring). These  $\Delta_L$  values were derived earlier<sup>2</sup>, assuming normal delocalization (compare Fig. 7, ref. 2). Similar changes in ring adsorption energy  $\Delta\sigma$  due to electronic activation by *i* should be approximately proportional to the average HAMMETT sigma function<sup>11</sup> for *meta* and *para* substituents on a benzene ring ( $\bar{\sigma}$ ) and to the adsorption energy of the ring after

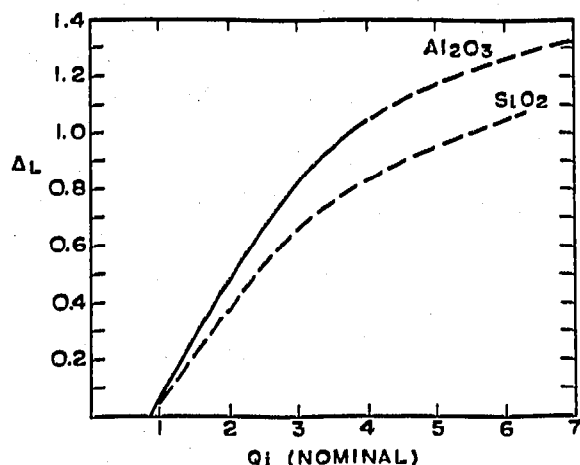


Fig. 1. Ring delocalization energy in solutes of type  $C_6H_5-i$ . —  $Al_2O_3$  (ref. 2); ---  $SiO_2$ ; equal values for  $Al_2O_3$  corrected for smaller adsorption energy of the benzene ring on silica ( $\times 1.50/1.86$ ).

delocalization by  $i$  (*i.e.*  $1.86 - \Delta_L$  for alumina,  $1.50 - \Delta_L$  for silica). From the increase in ring adsorption energy of the alkylbenzenes as a result of substitution by alkyl groups<sup>7</sup> we estimated that  $\Delta_\sigma$  equals  $-0.31 (1.86 - \Delta_L) \bar{\sigma}$  for alumina and  $-0.31 (1.50 - \Delta_L) \bar{\sigma}$  for silica. Finally the net (actual) adsorption energy of an aromatic group  $i$ , corrected for ring activation and delocalization, is given by Eqn. (1):

$$Q_i^\circ(\text{net}) = Q_i^\circ(\text{nominal}) + \Delta_L - \Delta_\sigma \quad (1)$$

Values of the net adsorption energies of the various aromatic groups of Table I are tabulated there. The differences in adsorption energies of aliphatic and aromatic (net) groups are also given in Table I, and these are seen to be constant within each of the three classes:  $1.38 \pm 0.15$  for class I;  $0.38 \pm 0.38$  for class II;  $0.59$  for class III. Within each class these differences show no dependence on the group adsorption energy.

Simple steric interference by an attached phenyl group to the adsorption of  $i$  should lead to a difference between net  $Q_i^\circ$  values for aliphatic and aromatic groups which is proportional to the size of  $Q_i^\circ$ . This is true of the *ortho-i*-toluenes<sup>1</sup> and of various di-aza-aromatics<sup>9</sup>, and is also theoretically reasonable. The complete absence of any such correlation for the data of Table I therefore discounts the relative importance of simple steric interference to adsorption by an attached phenyl group. The extent of conjugation of the group  $i$  with the aromatic ring is expected to vary widely among the groups of Table I; however, relative conjugation should be generally more important for groups with double bonds (*i.e.* class II) than for groups without. This should lead to greater loss in adsorption energy for the unsaturated groups (class II). The opposite of this prediction is actually noted, so that simple conjugation as an explanation for these  $Q_i^\circ$  value differences also appears unsatisfactory. We believe that the actual origin of these differences in  $Q_i^\circ$  values arises from a difference in preferred orientations of the various groups with the adsorbent surface. It is proposed that unsaturated groups such as cyano or aceto (class II) prefer to lie in the plane of the adsorbent surface, with polarization (or bond formation) of the group  $\pi$ -electrons in the perpendicular direction by the adsorbent surface field. Since the aromatic ring (*i.e.*

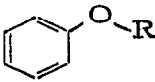

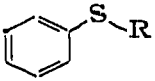

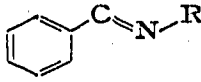

benzene) attached to such groups also prefers to lie in the plane of the adsorbent surface<sup>13</sup>, and since in *i*-phenyl compounds of this type it is possible for both groups to lie in the surface plane simultaneously, little loss in adsorption energy of *i* would result upon its attachment to a benzene ring. This is in fact observed; the average difference between aliphatic and net aromatic group adsorption energies for class II groups is small (within the S.D. from zero, in fact). In the case of saturated groups *i* such as the halogens and ethers (class I), it is suggested that the preferred orientation of the C—*i* bond is tilted to the plane of the adsorbent surface so as to permit a closer approach of *i* to specific sites, or a better alignment to the C—*i* bond with specific surface atoms (dipole interaction). This preferred orientation is of course not possible when *i* is attached to an aromatic ring. These different adsorbed configurations of the oxygen atom in aromatic and aliphatic ethers (class I) have in fact been invoked previously as an explanation for certain eluent anomalies (see Fig. 5, ref. 2).

The adsorption energy of the hydroxyl group (class III) may arise in part from hydrogen bonding by the alcohol proton to the adsorbent surface. Such hydrogen bonding would be less restricted by attachment of an aromatic ring to the hydroxyl group, relative to class I groups. This could account for the smaller difference in net adsorption energies of the aliphatic *versus* aromatic hydroxyl group.

The same trends in  $Q^{\circ}_i$  values upon substituting aromatic for aliphatic substituents on *i* are observed for further substitution of aromatic rings. This is illustrated in Table II, where corrected net  $Q^{\circ}_i$  values are compared for a few compound pairs of

TABLE II

FURTHER CORRELATION OF NET  $Q^{\circ}_i$  VALUES WITH THE POSITION OF *i* IN THE MOLECULE

Group	Structure	Net $Q^{\circ}_i$ *	Net $Q^{\circ}_i$ (aliph.) minus net $Q^{\circ}_i$ (arom.)
—O—		2.13	—
		1.04	1.09
—S—		1.54	—
		0.77	0.77
—N=		6.30**	—
		5.83	0.47

\* Ref. 9.

\*\* Assumes  $\sigma$ -ring twisted 90° from plane of —C=N—R, because of reduced hindrance to adsorption of —N= (ref. 10).

this type\*. We see in Table II that groups of class I (—O—, —S—) suffer a further substantial adsorption energy (0.77–1.09) loss in going from a mixed aliphatic, aromatic molecule to a fully aromatic molecule, while the one group of class II (—N=) shows a smaller adsorption energy difference for this same change (0.47, which is close to the average value of Table I for other class II groups).

The constancy of  $Q^{\circ}_i$  value differences between aromatic and aliphatic groups within each class of Table I permits us to accurately estimate aliphatic or aromatic  $Q^{\circ}_i$  values from the opposite type using Eqn. (1) and the average values of the adsorption energy difference: 1.4 (class I); 0.4 (class II); 0.6 (class III). The fact that this correlation fits data for both alumina and silica equally well suggests that it is also applicable for other metal oxide adsorbents.

#### $Q^{\circ}_i$ values on alumina versus silica

It has been shown previously<sup>7,8</sup> that the  $Q^{\circ}_i$  values for a particular group adsorbed on alumina, silica, and Florisil are generally, but not always, similar. Table III summarizes  $Q^{\circ}_i$  values for 27 different groups adsorbed on both alumina and silica. The alumina  $Q^{\circ}_i$  values are plotted *versus* the silica values in Fig. 2. It is apparent that a number of groups vary widely in their relative adsorption energies on the two adsorbents. The larger differences are classifiable into two categories: acidic groups

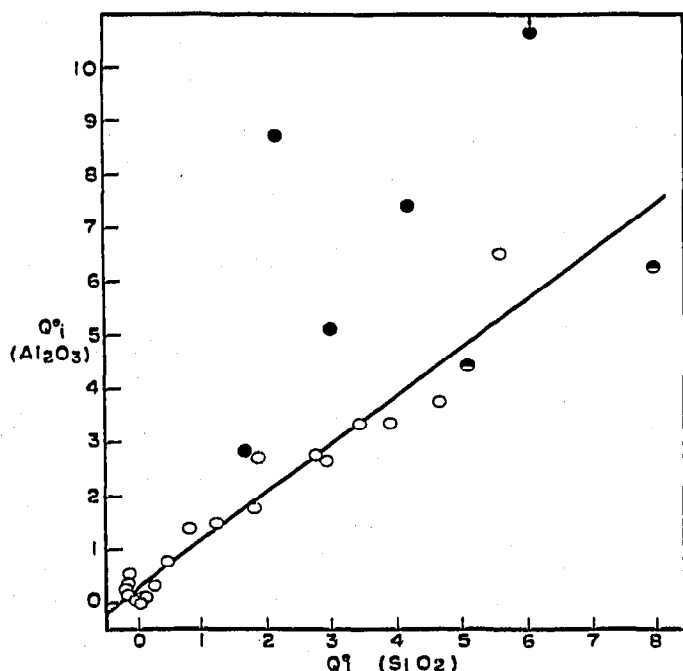


Fig. 2. Correlation of  $Q^{\circ}_i$  values on alumina *versus* those on silica. (●) acidic groups; (◐) basic groups; (○) neutral groups.

(closed circles) all show higher adsorption energies on alumina, while basic groups (half closed circles) show higher adsorption energies on silica. These deviations are in fact consistent with the commonly accepted descriptions<sup>14</sup> of alumina as "basic" and silica

\* Additional data of this same type are available for molecules with more than one ring (*e.g.* carbazole, fluorenone), but other complications (*e.g.* steric interference to adsorption) are present in these cases, preventing a simple interpretation of  $Q^{\circ}_i$  values.

TABLE III  
CORRELATION OF  $Q^{\circ}_t$  VALUES FOR ALUMINA AND SILICA

Group	Ref.*	$Q^{\circ}_t$		$\Delta Q^{\circ}_t$	$pK_A$ of group**	$pK_B$ of group**
		Silica	Alumina			
Ar)—Cl	a, b	-0.20	0.20			
Ar)—Br	a, b	-0.17	0.33			
Ar)—F	a, b	-0.15	0.11			
Ar)—I	a, b	-0.15	0.51			
R)—CH <sub>2</sub> —	c	-0.05	0.02			
Ar)—CH <sub>2</sub> —	c	0.01	0.07			
R)—CH <sub>3</sub>	c	0.05	-0.03			
Ar)—CH <sub>3</sub>	c	0.11	0.06			
Ar)—CH= (Ar)	a, b	0.25	0.30			
Ar)—S—(Ar)	b, d	0.48	0.76			
Ar)—SH	d, h	0.67	8.70	7.85	7	
Ar)—N(CH <sub>3</sub> )—(Ar)	d, e	0.96	1.37			
Ar)—S—R	a, f	1.29	1.32			
R)—SH	g, d	~ 1.70	2.80	1.02	11	
Ar)—O—R	a, f	1.83	1.77			
R)—S <sub>2</sub> —(R)	g, d	~ 1.90	2.70			
Ar)—NO <sub>2</sub>	a, f	2.77	2.75			
R)—S—(R)	a, b	2.94	2.65			
Ar)—NH—(Ar)	a, e	3.00	5.10	2.15	12	
Ar)—CO <sub>2</sub> —(R)	a, f	3.45	3.32			
Ar)—CHO	a, f, i	3.90	3.35			
Ar)—CO—(R)	a, f	4.69	3.74			
Ar)—OH	a, h, i	4.20	7.40	3.37	9.9	
Ar)—NH <sub>2</sub>	a, f	5.10	4.41	0.48		9.3
R)—OH	a, h, i	5.60	6.50			
Ar)—COOH	a, d, i	6.10	> 10.6	> 4.9	4.2	
R)—NH <sub>2</sub>	a, i, j	8.00	6.4 ± 0.4	1.2		3.2

\* (a) ref. 7; (b) ref. 5; (c) ref. 16; (d) experimental section; (e) ref. 10; (f) ref. 6; (g) approximate values estimated from relative adsorption strength values of ref. 17; (h) ref. 2; (i) ref. 4; (j) alumina value estimated from Table I, assuming difference in aliphatic and aromatic  $Q^{\circ}_t$  values is between the values for class I and class III.

\*\* Ref. 15.

as "acidic". If acidic and basic groups are ignored, it is found that the alumina and silica  $Q^{\circ}_t$  values can be correlated with a standard deviation of only  $\pm 0.43$  units by means of Eqn. (2):

$$Q^{\circ}_t (\text{alumina}) = 0.90 Q^{\circ}_t (\text{silica}) + 0.25 \quad (2)$$

This relationship can be inverted to permit silica group adsorption energies to be estimated from values for alumina:

$$Q^{\circ}_t (\text{silica}) = 1.11 Q^{\circ}_t (\text{alumina}) - 0.28 \quad (2a)$$

It has been shown previously<sup>8</sup> that  $Q^{\circ}_t$  values for adsorption on silica and Florisil are equal, when the standard activity for Florisil ( $\alpha = 1.00$ ) is chosen for 1% H<sub>2</sub>O-

Florisil (see ref. 16). Consequently  $Q^\circ_i$  values for aromatic and aliphatic groups adsorbed on Florisil may be derived from corresponding data for either alumina or silica. Similarly, aliphatic  $Q^\circ_i$  values for Florisil may be calculated from aromatic values just as in the case of alumina and silica.

The excess adsorption energies of acidic groups on alumina can be correlated with the acid strength or  $pK_A$  value of the group. Table III summarizes values of these group excess adsorption energies  $\Delta Q^\circ_i$  on alumina for acidic groups;  $\Delta Q^\circ_i$  equals experimental  $Q^\circ_i$  value minus value calculated from Eqn. (2). Similar group excess adsorption energies are also listed in Table III for the adsorption of bases on silica, using Eqn. (2a). Fig. 3 shows a plot of  $\Delta Q^\circ_i$  versus  $pK_A$  for acidic groups on alumina. In addition to the  $\Delta Q^\circ_i$  values of Table III similar values for the substituted phenols (dark circles) from a previous study<sup>2</sup> are included. These latter values are calculated relative to phenol (on alumina). It is clear from the data of Fig. 3 that the preferential adsorption ( $\Delta Q^\circ_i$  value) of acidic compounds on alumina is greater, the more acidic is the compound. If we assume that the surface of alumina behaves as a base of definite pH, which is capable of ionizing acid adsorbates SH according to the scheme  $SH \rightarrow S^- + H^+$ , and if we assume that the equilibrium constant for this reaction is the same as in water, then the relative concentrations of SH and of  $S^-$  on the alumina surface may be calculated as a function of  $pK_A$  and the  $H^+$  concentration on the alumina surface ( $H^+$ ):

$$\frac{(SH)}{(SH) + (S^-)} = \frac{10^{pK_A} (H^+)}{10^{pK_A} (H^+) + 1} \equiv f_{SH}.$$

We will assume that the acid SH consists of a single functional group  $i$ , for purposes of simplicity, although this does not detract from the generality of the present argument. In the absence of ionization of SH (*i.e.* normal adsorption, as on silica) it may be shown that for an adsorbent of activity  $\alpha$ ,  $\alpha Q^\circ_i = \log (SH)_a / (SH)_s V_a$ .  $(SH)_a$  and  $(SH)_s$  refer to undissociated SH in adsorbed and solution phases, respectively, and  $V_a$  is the adsorbent surface volume (see ref. 5). With dissociation of SH on the alumina surface, the group adsorption energy  $\alpha Q^\circ_i$  is equal to  $\log [(SH)_a + (S^-)_a] / (SH)_s V_a$ . The excess adsorption energy of  $i$ ,  $\Delta Q^\circ_i$ , is then given as  $1/\alpha$  times the difference in these two values of  $\alpha Q^\circ_i$  (*i.e.* the value for dissociation minus the value for no dissociation), which is equal to  $-(1/\alpha) \log f_{SH}$ . The term  $\Delta Q^\circ_i$  is then given as:

$$\Delta Q^\circ_i = -(1/\alpha) \log \left[ \frac{10^{pK_A} (H^+)}{10^{pK_A} (H^+) + 1} \right] \tag{3}$$

For small values of  $pK_A$ , Eqn. (3) simplifies to:

$$\Delta Q^\circ_i = \frac{pK_A - pH}{\alpha} \tag{3a}$$

where pH refers to the pH of the alumina surface, and  $pK_A$  is the acidity of the adsorbate. The data of Fig. 3 suggest a value of 12 for the pH of the alumina surface, and the dashed curve of Fig. 3 is calculated from Eqn. (3) with pH equal 12. The calculated curve provides a reasonable fit to the experimental data of Fig. 3.

The similar correlation of the excess adsorption energies of bases adsorbed on



silica with  $pK_B$  is shown in Fig. 4. The  $\Delta Q^\circ_i$  value for aniline ( $-0.48$ ) is essentially within the standard deviation of Fig. 2, Eqn. (2a), so we cannot decide *a priori* whether aniline actually exhibits a greater than normal affinity for the silica surface. The theoretical curve, analogous to Eqn. (3), drawn through the point in Fig. 4 for a primary aliphatic amine assumes a pH for the silica surface equal 4. From this it appears that bases with  $pK_B$  greater than 5 (*e.g.* aniline) do *not* preferentially adsorb on the silica surface.

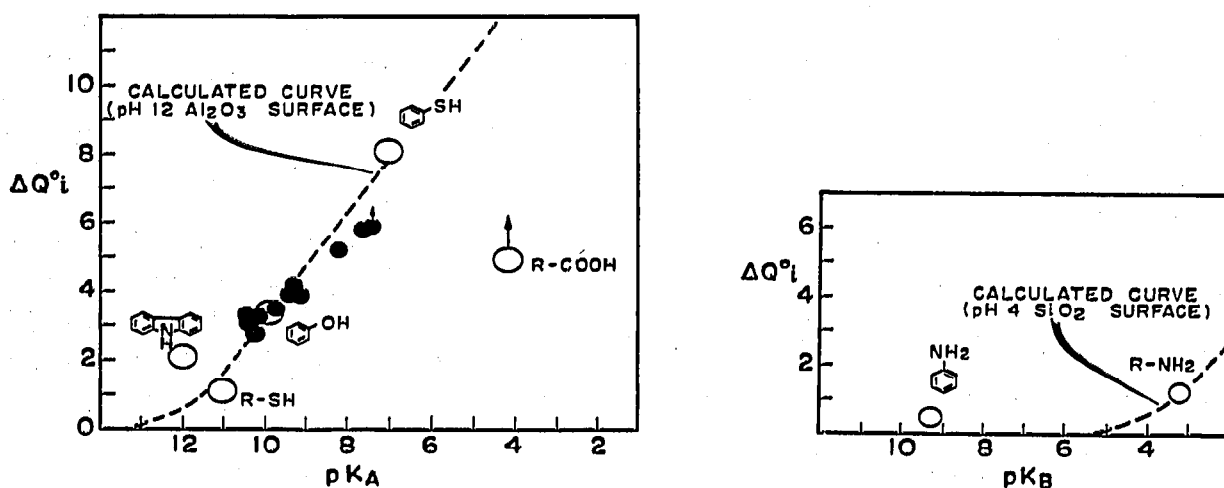


Fig. 3. Excess adsorption energies of acidic groups on alumina *versus*  $pK_A$ . (●) substituted phenol values<sup>2</sup>.

Fig. 4. Excess adsorption energies of basic groups on silica *versus*  $pK_B$ .

The above pH values for the alumina and silica surfaces are in agreement with other measures of the relative acidity or basicity of these surfaces. Thus the ionization constant of silicic acid  $H_3SiO_3$  is equal to  $10^{-10}$  (ref. 18) and the pH of a 1 M solution is approximately 5, in good agreement with the pH value of the silica surface (*i.e.* 4) inferred from Fig. 4. Similarly the basicity of alumina is assumed due to surface oxide ions, whose basicity should be similar to aluminate ion. The ionization constant of aluminic acid  $H_3AlO_3$  is  $4 \cdot 10^{-13}$  (ref. 18), and the pH of a 1 M solution of aluminate ion is approximately 12.4, again in good agreement with the pH of the alumina surface (*i.e.* 12) inferred from Fig. 3.

Bases have been claimed to preferentially adsorb on Florisil, but presently available data do not permit an estimate of the importance of this effect.

#### *Fundamental basis of group adsorption energies on the metal oxides*

Apart from the special case of adsorption of acidic groups on basic adsorbents, and *vice versa*, it is apparent that group adsorption energies stand in the same relative order on alumina, silica, Florisil, and (probably) other metal oxides and hydroxides. This suggests a similar mechanism of adsorption for isolated polar functional groups on all polar adsorbents. The previous correlational relationships permit us to reduce a large number of group  $Q^\circ_i$  values for different adsorbents and substituent types to a single basis (or standard state) for examination of the major molecular forces responsible for the adsorption of each group on a metal oxide surface. Table IV provides such

a summary of standard state  $Q^\circ_i$  values  $(Q^\circ_i)_s$ , for the adsorption of aliphatic groups on alumina. These  $(Q^\circ_i)_s$  values are corrected for the preferential adsorption of acids on alumina (*i.e.*  $\Delta Q^\circ_i$  is subtracted out). The average  $(Q^\circ_i)_s$  values of Table IV show a standard deviation from the individual values of only  $\pm 0.3$  units, implying an accuracy in  $(Q^\circ_i)_s$  of about  $\pm 5-10\%$ .

TABLE IV  
STANDARD STATE GROUP ADSORPTION ENERGIES

Group <sup>a</sup>	$(Q^\circ_i)_s^b$		Alumina		$\mu^c$	$E_B^d$
	Silica		Alumina			
	aliph.	arom.	aliph.	arom.	avg.	
C=C		0.81		0.62	0.71	~ 0.0
—F		1.65		1.64	1.64	1.46
—Cl		1.65	1.82	1.78	1.75	1.58
—Br		1.69	2.00	1.95	1.88	1.54
—I		1.69	2.00	2.10	1.93	1.30
—SH	1.78	2.23			2.00	1.30
—S—S—	1.95		2.70		2.32	
—S—	2.90	3.09	2.65	2.95	2.90	1.30
—O—		3.71	3.50	3.54	3.58	1.25
—N< <sup>e</sup>				4.40	(4.40)	
—CHO		5.21		4.73	4.97	2.76
—NO <sub>2</sub>		5.16	5.40	5.18	5.25	3.98
—C≡N			5.00	4.77	4.88	3.90
—CO <sub>2</sub> —		4.76	5.00	5.00	4.87	1.83
—CO—				4.75		
—CO—		6.08	5.00	5.23	5.44	2.89
—OH	5.60	5.72	6.50		5.92	1.60
—C=N—				6.30	6.30	0.50
—NH <sub>2</sub>		7.20		6.84	7.02	1.53
—SO—			6.70		6.70	4.03
—COOH		7.42			7.42	1.64
—CONH <sub>2</sub>				9.34	9.34	

<sup>a</sup> Substituted by aromatic or aliphatic substituents as noted.

<sup>b</sup> Aliphatic substituent on alumina basis; original  $Q^\circ_i$  values converted first to alumina basis, then to aliphatic basis.

<sup>c</sup> Dipole moments of compounds  $\sigma$ -*i* in solution; data of refs. 19 and 20.

<sup>d</sup> "Hard" base parameters; data of ref. 21.

<sup>e</sup> Probable steric hindrance in original compound (N,N-dimethylaniline).

Many different types of bonding between polar adsorbents and adsorbates have been proposed to explain the differing adsorption energies of various organic compounds: electrostatic interaction of adsorbate dipoles with the electric field of the adsorbent, hydrogen bonding between adsorbate and adsorbent, charge transfer complexation of adsorbent and adsorbate, etc. CHESSICK *et al.*<sup>22</sup> observed that the adsorption energies of various polar groups on rutile, corrected for dis-

persion forces\*, are proportional to their dipole moments. This suggests a major role for simple electrostatic forces in adsorption. The extension of this proposition to the group adsorption energies of Table IV is tested in Fig. 5, where  $(Q^\circ)_s$  is plotted *versus* group dipole moment  $\mu$ . It is clear, at least for many of the groups of Fig. 5, that group dipole moment by itself cannot account for the total group

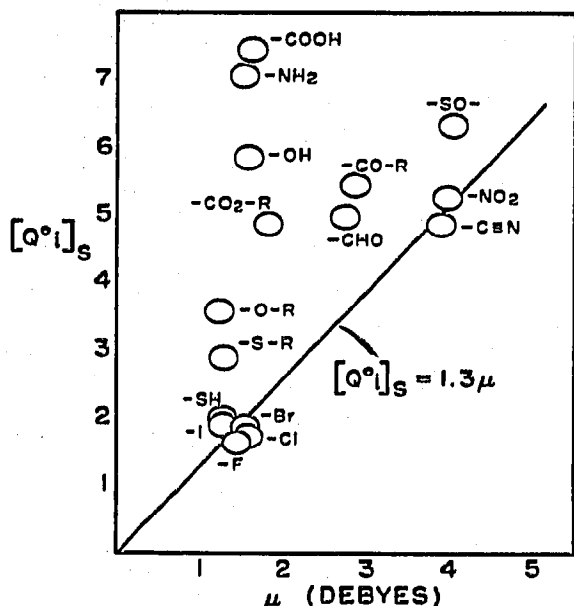


Fig. 5. Standard state group adsorption energies *versus* group dipole moment.

adsorption energy. The maximum possible contribution of group dipole moment to adsorption energy is given by the solid line of Fig. 5 through the lower points. Since this line accurately correlates 7 out of the 16 points of Fig. 5, it is tempting to assume that these 7 groups adsorb by aligning their dipoles with the adsorbent surface field, with most of the group adsorption energy resulting from this interaction.

The various groups that lie above the lower line of Fig. 5 are all recognizable as being more basic than the 7 points on the line (in the sense of being better able to hydrogen bond with a proton donor, for example). This suggests an alternative adsorption mechanism, relative to dipole interaction, involving weak bond formation between a basic adsorbate group  $i$  and an acidic adsorbent group. Such an acid-base interaction is not to be confused with complete ionization of the group by proton addition or subtraction, as in the adsorption of acids on alumina, and bases on silica. Weak acid-base interactions without proton transfer have recently been treated quantitatively by DRAGO AND WAYLAND<sup>21</sup>. These authors propose that the heat of such reactions can be expressed by a four parameter equation which recognizes both "hard" and "soft" interactions between the acid and base involved:

$$-\Delta H = E_A E_B + C_A C_B \quad (4)$$

— $\Delta H$  refers to the heat of reaction of the acid and base,  $E_A$  and  $C_B$  are parameters

\* The group adsorption energies of Table IV are essentially on this basis, since they represent the adsorption energy of the group minus that of an equivalent part of a pentane molecule; dispersion forces should roughly cancel in this subtraction.

which are proportional to the relative acidity of "hard" and "soft" acids, and  $E_B$  and  $C_B$  are proportional to the relative basicities of "hard" and "soft" bases, respectively. Actually every acid and base simultaneously possesses both "hard" and "soft" character, "hard" referring primarily to electrostatic interactions as in hydrogen bonds and "soft" referring to covalent interactions as in iodine complexes with bases. Since heats and free energies of adsorption from solution have been noted to be approximately equal<sup>16</sup>,  $(Q^\circ_i)_s$  could be substituted for  $-\Delta H$  in Eqn. (4) for those cases where similar acid-base interactions describe the adsorption of  $i$ . To a first approximation Eqn. (4) for adsorption can be split into two limiting relationships for those cases which can be cleanly classified as either "hard" or "soft" interactions:

$$\text{(hard)} (Q^\circ_i)_s = E_A E_B \quad (5)$$

$$\text{(soft)} (Q^\circ_i)_s = C_A C_B \quad (5a)$$

This is a necessary simplification in attempting to treat adsorption reactions, since both "hard" and "soft" acid sites may exist separately on the adsorbent surface, with their relative importance as adsorption sites varying with whether a "hard" or "soft" adsorbate group is involved.

Comparison of the  $(Q^\circ_i)_s$  values of Table IV with Eqns. (5) and (5a) suggests that acid-base interactions, if they contribute significantly to group adsorption energy, are predominantly "hard" in character; *i.e.* Eqn. (5) applies. The latter relationship is tested in Fig. 6 for those groups whose  $E_B$  values have been reported<sup>21</sup>. A fairly

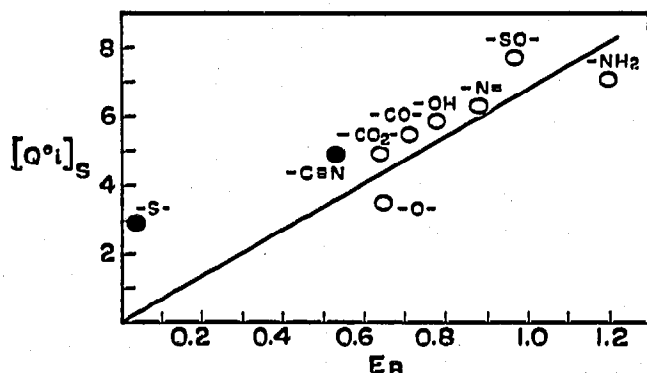


Fig. 6. Standard state group adsorption energies *versus* group basicity.

reasonable correlation is noted ( $\pm 0.8$  unit in  $Q^\circ_i$ ), with the exception of the sulfide group ( $-\text{S}-$ ). Possibly the sulfide group adsorbs as a "soft" base on a different adsorbent site, since this group is predominantly "soft" in character relative to the other groups of Fig. 6. The point for the cyano group is also somewhat high, and this may reflect adsorption of this group by a dipole-adsorbent surface field interaction (*i.e.* purely electrostatic), rather than by an acid-base interaction. However, both of these processes are predominantly electrostatic in origin, and it may be meaningless to attempt to differentiate them. Tentatively we assume that three different adsorption mechanisms are available to a polar group: (i) dipole-adsorbent surface field interactions, with  $(Q^\circ_i)_s$  equal  $1.3 \mu$ ; (ii) adsorption as a "hard" base on a "hard" acid site, with  $(Q^\circ_i)_s$  equal  $6.8 E_B$ ; (iii) adsorption as a "soft" base on a "soft" acid site, with

TABLE V

GROUP ADSORPTION ENERGIES FOR ALUMINA, SILICA AND FLORISIL

Group	$Q^{\circ}_i$								
	Alumina			Silica			Florisol*		
	$X, Y=Ar$	$X=Al$ $Y=Ar$	$X, Y=Al$	$X, Y=Ar$	$X=Al$ $Y=Ar$	$X, Y=Al$	$X, Y=Ar$	$X=Al$ $Y=Ar$	$X, Y=Al$
X-CH <sub>3</sub> methyl	0.06	—	-0.03	0.11	—	0.07	0.10	—	-0.01
X-CH <sub>2</sub> -Y methylene	0.12	0.07	0.02	0.07	0.01	-0.05	0.19	0.10	0.01
X-Cl chloro	0.20	—	1.82	-0.20	—	1.32	-0.20	—	1.74
X-F fluoro	0.11	—	1.64	-0.15	—	1.30	-0.15	—	1.54
X-B bromo	0.33	—	2.00	-0.17	—	1.32	-0.17	—	1.94
X-I iodo	0.51	—	2.00	-0.15	—	1.28	-0.15	—	1.94
X-SH mercapto	8.70	—	2.80	0.67	—	1.70	0.67	—	1.70
X-S-S-Y disulfide	?	~ 1.1	2.70	?	0.94	1.90	?	0.94	1.90
X-S-Y sulfide	0.76	1.32	2.65	0.48	1.29	2.94	?	1.30	2.94
X-O-Y ether	1.04	1.77	3.50	0.87	1.83	3.61	0.87	1.81	3.61
X-N-Y tertiary amine	?	2.48	4.40	?	2.52	~ 5.8	?	?	?
X-CHO aldehyde	3.35	—	4.73	3.48	—	4.97	3.35	—	4.97
X-NO <sub>2</sub> nitro	2.75	—	5.40	2.77	—	5.71	3.07	—	5.71
X-C≡ nitrile	3.25	—	5.00	3.33	—	5.27	3.33	—	5.27
X-CO <sub>2</sub> -Y ester	4.02	3.40	5.00	4.18	3.45	5.27	4.18	3.45	5.27
X-CO-Y keto	4.36	3.74	5.00	4.56	4.69	5.27	4.56	4.32	5.27
X-OH hydroxyl	7.40	—	6.50	4.20	—	5.60	4.20	—	5.60
X-C=N-Y imine	4.14	4.46	6.00	?	?	?	?	?	?
X-NH <sub>2</sub> amino	4.41	—	6.24	5.10	—	8.00	?	?	?
X-SO-Y sulfoxide	?	4.0	6.70	?	4.2	7.2	?	4.2	7.2
X-COOH carboxylic acid	19	—	21	6.1	—	7.6	6.1	—	7.6
X-CONH <sub>2</sub> amide	6.2	—	8.9	6.6	—	9.6	6.6	—	9.6
-C= aromatic carbon	0.31	0.31	0.31	0.25	0.25	0.25	0.18	0.18	0.18

\* Assumes  $\alpha = 1.00$  for 1% H<sub>2</sub>O- Florisol (see ref. 16).

$(Q^{\circ}_i)_s$  equal  $0.37 C_B$  (from the adsorption energy of the sulfide group). That mechanism which gives the largest value of  $(Q^{\circ}_i)_s$  is assumed to predominate, so that  $(Q^{\circ}_i)_s$  can be predicted when the values of  $\mu$ ,  $E_B$ , and  $C_B$  for a group are available.

GILES<sup>23</sup> has suggested that hydrogens in such groups as —OH, —SH,  $>NH$ , and —CHO may adsorb on alumina by hydrogen bonding to the adsorbent. If true this should manifest itself by anomalously high  $(Q^{\circ}_i)_s$  values for such groups. As seen in Fig. 5 (—SH) and Fig. 6 (—OH, —NH<sub>2</sub>), no such enhancement of the adsorption energies of these groups is evident. With the exception of groups with  $pK_A$  values less than 12, we conclude that hydrogen bonding of group protons to the adsorbent is unimportant in contributing to group adsorption energy.

Regardless of the actual fundamental interpretation of the data of Table IV these  $(Q^{\circ}_i)_s$  values can be used to predict nominal group adsorption energies for a wide range of groups on each of the present three adsorbents. Table V summarizes these predicted and measured values, the experimental values being given where available.

#### ACKNOWLEDGEMENT

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#### SUMMARY

Functional group adsorption energies  $Q^{\circ}_i$  for adsorption of a sample on alumina, silica, Florisil, and (presumably) other metal oxide adsorbents can now be correlated in terms of a single theoretical model. Given a value of  $Q^{\circ}_i$  for the adsorption of a polar group  $i$  on any of these three adsorbents it is possible to predict reliable  $Q^{\circ}_i$  values for the same group on the other two adsorbents. Furthermore, given  $Q^{\circ}_i$  values for the group  $i$  substituted either by an aromatic or an aliphatic substituent, it is possible to calculate  $Q^{\circ}_i$  for the opposite case. This in turn permits the calculation of numerous solute adsorption energies and eluent strength values that were previously unavailable. A number of group adsorption energies are now available in a standard state for interpretation in terms of the fundamental molecular processes which give rise to selective adsorption. The present correlations throw additional light on the general mechanisms of adsorption of polar compounds on the metal oxide adsorbents. Alumina preferentially adsorbs acids with  $pK_A$  values less than 13, relative to silica and Florisil, while silica appears to preferentially adsorb bases with  $pK_B$  values less than 5.

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