1002 © *1983 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *56*, *1002—1005 (1983)* [Vol. 56, No. 4

Prediction of Adsorbability of Organic Compounds from Aqueous Solution on Activated Carbon by Means of the Linear Free-energy Relationship

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(Received August 16, 1982)

A method is presented for predicting the adsorbability of a wide variety of organic compounds from aqueous solution onto an activated carbon. The method, which is based on the linear free-energy relationship, requires only the solute's molecular refraction and the number of hydrophilic functional groups. The molecular refraction represents the free energy contribution by the solute-adsorbent interaction and the number of hydrophilic functional groups represents that by the solute-solvent interaction.

The ability to predict the adsorbability for a given adsorbent from a knowledge of the physical properties of the adsorbate is an important objective in adsorbent-adsorbate interaction research. In our preceding papers,[1-5] the methods for prediction of the adsorption isotherms of organic compounds from aqueous solution onto activated carbons were discussed. The adsorption isotherms of aliphatic monofunctional compounds,[3] amino acids,[4] and saccharides[5] could be predicted from the molecular refraction alone. The prediction method was applicable to activated carbons with different adsorptive capacities. Manes *et al.* applied the Polanyi adsorption potential theory to adsorption from solution onto activated carbon.[6-8] The Polanyi methods of predicting adsorption isotherms requires the solute's solubility, refractive index, and molar volume. McGuire and Suffet, using the separable formalism of the partial solubility parameters, defined a net adsorption energy for the adsorption of solute from a dilute solution onto adsorbent.[9] The method requires the solute's solubility parameter and molar volume.

Here we describe a method using the linear free-energy relationships which are widely used as tools for investigating chemical similarity.[10]

Experimental

The adsorbent used (Pittsburgh Activated Carbon Co., grade CAL activated carbon) and the experimental techniques were the same as described in a previous paper.[11] All of the adsorbates came from commercial sources (stated minimum assay 99%) and were used without further purification.

Results and Discussion

The adsorption equilibria of 57 organic compounds from aqueous solution onto CAL activated carbon at 25 °C were measured. Table 1 shows the amount adsorbed, k(mg/g), at very low equilibrium concentration, 1 mg/l, including data for 45 compounds from the literatures.

By assuming that the adsorbed molecules behave ideally at the low concentration, the Gibbs free energy change for the adsorption process, ΔG, is calculated experimentally by the following equation:

$$\Delta G = -RT\ln(k/V), \qquad (1)$$

where V is the volume of adsorption phase (pore volume).[11-13] This equation indicates that the value

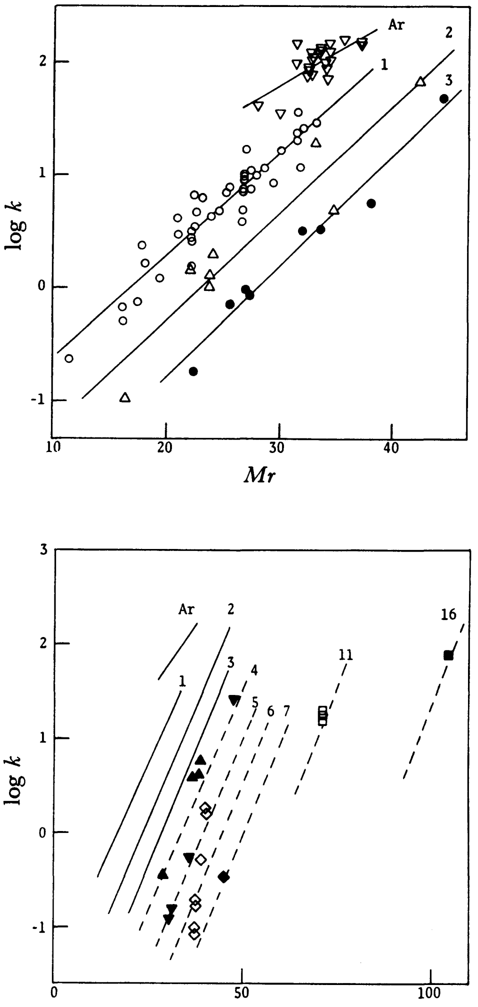

Fig. 1. Relationship between log k and molecular refraction. The values in figure are the number of hydrophilic functional group, Nf. The lines 1—3 and Ar (aromatics) are from linear least-squares analysis of the data points. $Nf=1$: $\log k=0.09125Mr-1.530$ ($r=0.9259$, $s=0.1882$, $F=240.3$, $t=15.50$***), $Nf=2$: $\log k=0.09521Mr-2.185$ ($r=0.9375$, $s=0.3253$, $F=43.58$, $t=6.601$***), $Nf=3$: $\log k=0.09899Mr-2.773$ ($r=0.9751$, $s=0.1769$, $F=115.8$, $t=10.76$***), Ar: $\log k=0.05885Mr+0.04096$ ($r=0.6665$, $s=0.1360$, $F=17.59$, $t=4.194$***), $Nf=1$: ○; $Nf=2$: △; $Nf=3$: ●; $Nf=4$: ▲; $Nf=5$: ▼; $Nf=6$: ◇; $Nf=7$: ◆; $Nf=11$: □; $Nf=16$: ■; Ar: ▽.

Table 1. Amount adsorbed, k, of 102 organic compounds from aqueous solution onto CAL activated carbon at an equilibrium concentration, 1 mg/l, and number of hydrophilic functional groups, Nf, in an adsorbate molecule

Compound No.	Adsorbate	k/mg g^{-1}	Nf	Ref.
1	1-Propanol	0.745	1	11
2	1-Butanol	3.20	1	11
3	1-Pentanol	10.5	1	11
4	1-Hexanol	25.6	1	11
5	2-Methyl-1-propanol	2.75	1	
6	2-Butanol	2.49	1	
7	2-Methyl-2-propanol	1.48	1	
8	3-Methyl-1-butanol	9.58	1	
9	2-Pentanol	9.89	1	
10	3-Pentanol	6.67	1	
11	2,2-Dimethyl-1-propanol	3.66	1	
12	2-Methyl-2-butanol	6.91	1	
13	Cyclopentanol	4.69	1	
14	Cyclohexanol	7.93	1	
15	2-Methyl-1-butanol	8.98	1	
16	3-Methyl-2-butanol	4.76	1	
17	Acetaldehyde	0.229	1	11
18	Propionaldehyde	0.663	1	11
19	Butyraldehyde	3.15	1	11
20	Valeraldehyde	8.35	1	11
21	Propylamine	1.18	1	
22	Butylamine	4.21	1	
23	Pentylamine	11.9	1	
24	Hexylamine	28.2	1	
25	Methyl acetate	1.78	1	11
26	Ethyl acetate	3.60	1	11
27	Propyl acetate	12.0	1	11
28	Butyl acetate	26.5	1	11
29	Isopropyl acetate	7.04	1	
30	Isobutyl acetate	11.0	1	
31	Diethyl ether	5.14	1	11
32	Dipropyl ether	19.4	1	11
33	Acetone	0.484	1	11
34	2-Butanone	4.66	1	11
35	2-Pentanone	7.43	1	11
36	2-Hexanone	16.7	1	11
37	Cyclopentanone	6.71	1	
38	Cyclohexanone	9.96	1	
39	Propionic acid	2.59	1	11
40	Butyric acid	7.04	1	11
41	Valeric acid	19.2	1	11
42	Hexanoic acid	42.3	1	11
43	Glycine	0.0994	2	4
44	L-Leucine	4.84	2	4
45	2-Ethoxyethanol	2.17	2	
46	2-Butoxyethanol	22.0	2	
47	2-(Hexyloxy)ethanol	68.0	2	
48	1,4-Butanediol	0.978	2	
49	1,2-Butanediol	1.41	2	
50	1,4-Dioxane	1.59	2	
51	L-Glutamine	3.37	3	4
52	L-Threonine	0.953	3	4
53	L-Serine	0.175	3	4
54	L-Glutamic acid	3.47	3	4
55	L-Aspartic acid	0.943	3	4
56	L-Methionine	5.43	3	4
57	Diethylene glycol	0.783	3	
58	2-(2-Butoxyethoxy)-ethanol	52.9	3	
59	L-Histidine	6.44	4	4
60	2-Desoxy-D-ribose	0.360	4	5
61	Triethylene glycol	4.39	4	
62	Triethanolamine	4.56	4	
63	D-(+)-Xylose	0.162	5	5
64	D-(−)-Arabinose	0.132	5	5
65	L-(+)-Rhamnose	0.587	5	5
66	Tetraethylene glycol	29.2	5	
67	D-(+)-Glucose	0.185	6	5
68	D-(+)-Mannose	0.104	6	5
69	D-(−)-Fructose	0.0940	6	5
70	D-(+)-Galactose	0.202	6	5
71	α-Methyl D-glucoside	1.73	6	5
72	α-Methyl D-mannoside	1.95	6	5
73	D-(−)-Mannitol	0.570	6	5
74	Perseitol	0.371	7	
75	(+)-Maltose	19.8	11	5
76	(+)-Sucrose	18.3	11	5
77	(+)-Lactose	20.9	11	5
78	Raffinose	83.5	16	
79	Chlorobenzene	101	0	
80	Benzoic acid	77.2	1	
81	Phenol	37.7	1	
82	Aniline	32.4	1	
83	Anisole	109	1	
84	*o*-Methoxyphenol	130	2	
85	*m*-Methoxyphenol	101	2	
86	*p*-Methoxyphenol	158	2	
87	*o*-Nitrophenol	122	1	
88	*m*-Nitrophenol	128	1	
89	*p*-Nitrophenol	137	1	
90	*o*-Chlorophenol	103	1	
91	*m*-Chlorophenol	108	1	
92	*p*-Chlorophenol	135	1	
93	*o*-Cresol	90.3	1	
94	*m*-Cresol	76.1	1	
95	*p*-Cresol	84.3	1	
96	*o*-Hydroxybenzoic acid	65.0	2	
97	*m*-Hydroxybenzoic acid	83.9	2	
98	*p*-Hydroxybenzoic acid	99.0	2	
99	*o*-Hydroxyacetophenone	143	2	
100	*p*-Hydroxyacetophenone	135	2	
101	*m*-Aminophenol	158	2	
102	*p*-Bromophenol	166	1	

of log k may represent the adsorbability associated with the free energy change.

In the linear free-energy relationship models, the logarithm of activity is expressed as a linear function of physicochemical parameters. The method is based on multiple linear regression analysis. The expression for the free energy change of the adsorption process may be given by the following equation:

$$\Delta G = \Delta G_{\mathrm{js}} - \Delta G_{\mathrm{is}} - \Delta G_{\mathrm{ji}}, \qquad (2)$$

where ΔG is the net free energy change, ΔG_{js} is that associated with the solute-adsorbent interaction, ΔG_{is} the solvent-adsorbent interaction, ΔG_{ji} the solute-solvent interaction, and the subscripts i, j, and s refer to solvent, solute, and adsorbent, respectively. In the case of the adsorption from water, ΔG_{is} is identical for each adsorbate and consequently the following relation may be derived:

$$\Delta G = \Delta G_{js} - \Delta G_{ji} - \text{const.} \tag{3}$$

Each of these terms can be estimated with a knowledge of the physicochemical properties of each species. The ΔG_{js} term is mainly affected by the hydrophobic effect because the surface of activated carbon is hydrophobic. The driving force for the adsorption by hydrophobic effect is the dispersion component of the Van der Waals forces. This adsorptive interaction is strongly dependent on the polarizability of the solute. Since the polarizability of a molecule is proportional to the molecular refraction (Mr), ΔG_{js} can be expressed in terms of molecular refraction. Assuming that the ΔG_{ji} term is identical for each adsorbate, the following equation may be derived:

$$\log k = A_1 Mr + A_0, \tag{4}$$

where A_1 and A_0 are constant. Figure 1 shows a plot of log k *vs.* Mr for 102 organic compounds. A good linear relationship was obtained within each family of compounds with the same number of hydrophilic functional groups (Nf). The correlation coefficient(r) for compounds **1**—**42** with $Nf=1$ was 0.926, $r=0.938$ for compounds **43**—**50** with $Nf=2$, and $r=0.975$ for compounds **51**—**58** with $Nf=3$. The adsorbability of aliphatic compounds decreased with an increase in the number of hydrophilic functional groups in a solute molecule. This indicates that the ΔG_{ji} term in Eq. 3 affects the adsorbability.

The free energy change for the solution process was calculated by Amidon *et al.*.[14] The molecular surface area for 158 aliphatic hydrocarbons, olefins, alcohols, ethers, ketones, aldehydes, esters, and fatty acids were computed and correlated with the aqueous solubilities. The expression was:

$$\log S = \theta_1 \cdot TSA + \theta_2 \cdot IFG + \theta_0, \tag{5}$$

where S is the aqueous solubility, TSA is the total surface area, and IFG is the functional group index (zero for hydrocarbons and unity for a monofunctional compound). From the coefficients for the IFG term, the free energy contribution of functional group to the solution process (ΔG_{sol}) may be calculated. The values of ΔG_{sol} for each functional group are −4090—−4310 cal/mol. This suggests that for the functional groups (-OH, -O-, >C=O, -CHO, -COO-, and -COOH) the free energy contributions per one functional group to the ΔG_{ji} term is nearly equal. Therefore, the ΔG_{ji} term may be related to the number of the functional group regardless of the kind. Thus:

$$\log k = A_1 Mr + A_2 Nf + A_0, \tag{6}$$

where A_1, A_2, and A_0 are constant. The data of compounds **1**—**78** were given to a NEC PC-8001 computer to determine the A_1, A_2, and A_0 values by means of multiple regression analysis. The regression equation is:

$$\log k = 0.1089\, Mr - 0.4919\, Nf - 1.520. \tag{7}$$

The correlation coefficient r was 0.9355, the standard deviation s was 0.2596, the F-value representing the over-all goodness of fit was 262.7, and the t-values in the Student test were 22.87*** (for 0.1089) and −21.17*** (for −0.4919). The asterisk, ***, represents that the significant level of the regression coefficient is 0.1%. The results of statistical test indicate that Eq. 7 is statistically significant.

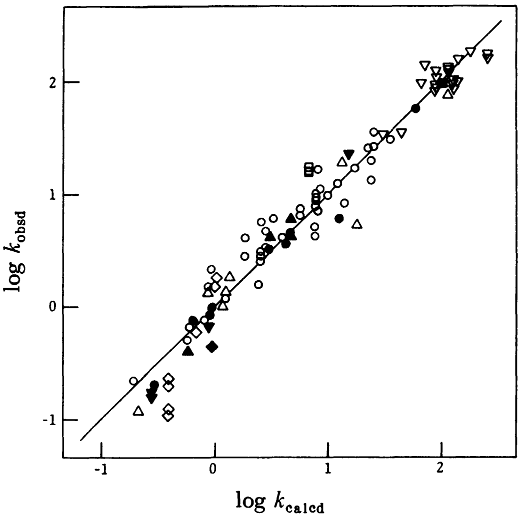

Fig. 2. Relationship between log k observed and log k calculated using Eq. 9.

It can be seen from Fig. 1 and Table 1 that the adsorbability of aromatic compounds is higher than the other compounds in spite of the presence of hydrophilic functional groups in a molecule. The phenomena can be explained by the electronic effects and the resonance effects. The solubility of aliphatic compounds increases markedly with an increase in the number of hydrophilic functional groups in a molecule, while the solubility of aromatic compounds does not appreciably increase because of the resonance effects. This suggests that the ΔG_{ji} term can not be related to Nf for aromatics. The high adsorbability of aromatics can be accounted for by the strong interaction with π-electrons in the graphitic structure of an activated carbon. Therefore, ΔG for aromatics must be distinguished from that for aliphatics. Equation 6 has been changed to the following equation:

$$\log k = A_1 \cdot Mr + A_2 \cdot D \cdot Nf + A_0, \tag{8}$$

where D is the dummy variable being zero for aromatics and unity for aliphatics. From the data of 102 compounds in Table 1, a statistical analysis yields the following results:

$$\log k = 0.1044\, Mr - 0.4694 D \cdot Nf - 1.450 \tag{9}$$

$$(r = 0.9642,\ s = 0.2409,\ F = 654.4,\ t(0.1044) = 33.85^{***},$$
$$t(-0.4694) = -34.29^{***}).$$

Figure 2 shows the relationship between log k observed and log k calculated using Eq. 9. These results indicate that the adsorbability of many compounds can be predicted from the molecular refraction and the number of hydrophilic functional group. Since the physical constants Mr and Nf can be easily obtained, the above method for predicting adsorbability is simpler and more accurate than the other methods.

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