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The Adsorption of Amino Acids from Water on Activated Carbons

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Freundlich's adsorption constants of 17 amino acids from aqueous solutions onto an activated carbon have been determined and correlated with various physical constants. A good linear relationship is obtained between the adsorption constants and such physical constants as the molecular refraction and the parachor. The adsorption isotherms of amino acids can be predicted from the molecular refraction or the parachor alone.

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 a previous paper,[1)] the partition coefficients of 93 organic compounds between an aqueous solution and activated carbon phases at an infinite dilution have been calculated and correlated with various physical constants. Further, the adsorptive mechanism on activated carbon in an aqueous solution has been discussed.[2)] Abe *et al.*[3,4)] have presented an adsorption equation for predicting the adsorption isotherms of organic compounds from water on activated carbons and showed that, for aliphatic monofunctional compounds, such physical constants as the molecular refraction or the parachor are useful for the prediction. The present paper aims to examine whether or not the method of prediction is applicable to such multifunctional compounds as amino acids.

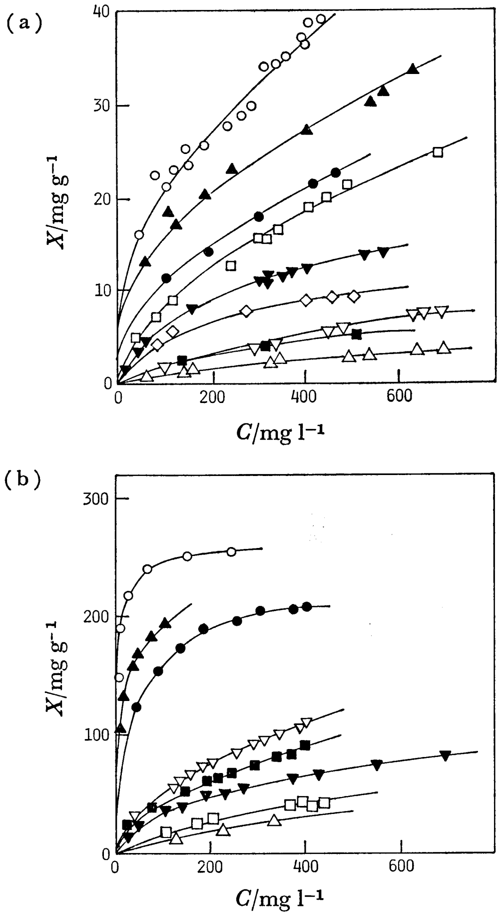

Fig. 1. Adsorption isotherms of 17 amino acids from water onto CAL activated carbon.

(a) ○: L-Glutamic acid, ▲: L-glutamine, ●: L-proline, □: DL-valine, ▼: L-asparagine, ◇: L-threonine, ▽: DL-alanine, ■: L-serine, △: glycine.

(b) ○: L-Tryptophan, ▲: L-tyrosine, ●: L-phenylalanine, ▽: L-methionine, ■: L-histidine, ▼: L-leucine, □: L-isoleucine, △: L-aspartic acid.

Experimental

The adsorbent (Pittsburgh Activated Carbon Co., grade CAL activated carbon) and experimental techniques were the same as those described in a previous paper.[2)] All of the adsorbates came from commercial sources (stated minimum assay 99%) and were used without further purification. The substances tested were adsorbed from pure solutions, with no special effort being made to control their pH, since ampholytes in solution tend to maintain pH values near their isoelectric points. A comparison of the pH values of many amino acid solutions before and after adsorption revealed relatively little change in the pH.

Results and Discussion

Figure 1 shows the adsorption isotherms of 17 amino acids onto CAL activated carbon at 25 °C. The adsorption isotherms have been approximated by means of the Freundlich equation:

$$\log X = \log k + \frac{1}{n} \log C, \qquad (1)$$

where C is the equilibrium concentration(mg/l), X is the amount of adsorption(mg/g), and k and $1/n$ are constants. The results of regression analysis using Eq. 1 are presented in Table 1.

In order to clarify the adsorptive mechanism of amino acids, the correlation between the adsorption constants and various physical constants has been examined. Table 2 shows the results of the regression analysis for Eq. 2:

$$\log k = a\Phi + b, \qquad (2)$$

where Φ is the physical constant of amino acids and where a and b are constants. In this table, r is the correlation coefficient; s, the standard deviation, and F and t, the values of the statistical test. A high correlation coefficient has been obtained for the molecular-size parameters, such as the molecular refraction, the parachor, or the molecular weight. This result resembles that observed for aliphatic monofunctional compounds.[4)] Further, a good linear relationship has been obtained for a very simple value, the carbon-atom number in a molecule. This suggests that the decisive component of the adsorption forces on an activated carbon surface is the hydrophobic interaction. It is well known that compounds with a low solubility are more readily adsorbed than compounds with a high solubility, but the data in Table 2 indicate that solubility is not a dominant factor governing the adsorption of amino acids. Figure 2 shows the relationship between log *k* and the molecular refraction.

Table 3 shows the results of regression analysis for Eq. 3:

$$1/n = a\Phi + b. \qquad (3)$$

The correlation coefficients for Eq. 3 are lower than those for Eq. 2. Figure 3 shows the relationship between $1/n$ and the molecular refraction.

Table 1. Adsorption parameters of amino acids on CAL activated carbon (25 °C)

Compound No.	Compound	*k*	$1/n$
1	Glycine	0.0994	0.523
2	DL-Alanine	0.0444	0.774
3	DL-Valine	0.697	0.541
4	L-Leucine	4.84	0.430
5	L-Isoleucine	1.67	0.519
6	L-Serine	0.175	0.534
7	L-Threonine	0.953	0.370
8	L-Tyrosine	62.4	0.247
9	L-Phenylalanine	61.3	0.207
10	L-Tryptophan	129	0.134
11	L-Aspartic acid	0.943	0.553
12	L-Asparagine	0.201	0.693
13	L-Glutamic acid	3.47	0.393
14	L-Glutamine	3.37	0.349
15	L-Histidine	6.44	0.423
16	L-Methionine	5.43	0.499
17	L-Proline	0.524	0.611

In order to examine whether Eqs. 2 and 3 are applicable to the other activated carbons with different adsorptive capacities, the data in two articles have been tested. Cheldelin and Williams[5] measured

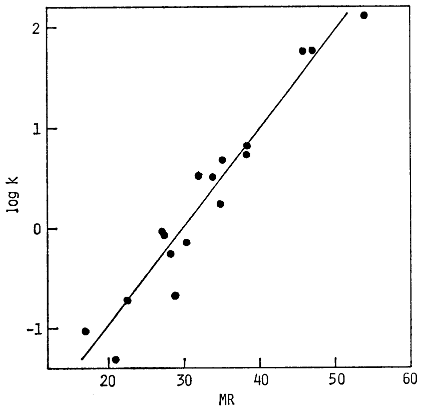

Fig. 2. Relationship between log *k* and molecular refraction (*MR*).

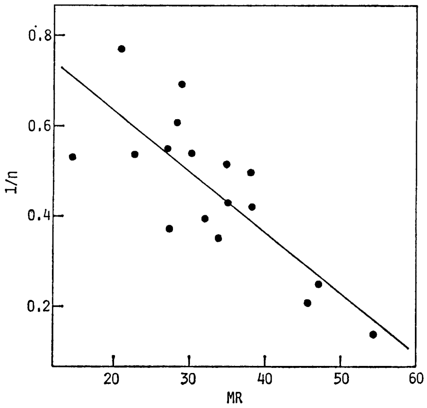

Fig. 3. Relationship between $1/n$ and molecular refraction (*MR*).

Table 2. Results of regression analysis for the $\log k = a\Phi + b$ equation

Physical constant	Φ	*a*	*b*	*r*	*s*	*F*	*t*
Molecular refraction[a]	*MR*	0.09802	−2.945	0.9575	0.2953	165.4	12.86***[d]
Parachor[b]	*P*	0.01341	−3.633	0.9514	0.3154	143.1	11.96***
Molecular weight	*MW*	0.02905	−3.635	0.9355	0.3620	105.1	10.25***
Carbon number	*CN*	0.3933	−1.839	0.9308	0.3743	97.31	9.865***
Solubility[c]	$\log C_s$	−0.7891	1.569	−0.6417	0.7855	10.50	−3.240**

a) These physical constants are taken from A. I. Vogel, W. C. Cresswell, G. H. Jeffery, and J. Leicester, *J. Chem. Soc.*, **1952**, 514. b) H. P. Meissner, *Chem. Eng. Progr.*, **45**, 149 (1949). c) The solubilities(C_s), in g/1000 g of water, are taken from "Seikagaku Data Book," ed by Nippon Seikagakukai, Tokyokagakudojin, Tokyo (1979), Vol. 1. d) Significance level: *<0.05, **<0.01, ***<0.001.

Table 3. Results of regression analysis for the $1/n = a\Phi + b$ equation

Physical constant	Φ	*a*	*b*	*r*	*s*	*F*	*t*
Molecular refraction	*MR*	−0.01356	0.9060	−0.7845	0.1072	24.01	−4.900***
Parachor	*P*	−0.001836	0.9958	−0.7717	0.1099	22.09	−4.700***
Molecular weight	*MW*	−0.004087	1.011	−0.7797	0.1082	23.26	−4.823***
Carbon number	*CN*	−0.05698	0.7672	−0.7990	0.1039	26.48	−5.145***
Solubility	$\log C_s$	0.1070	0.2853	0.5157	0.1481	5.435	2.331*

Table 4. Relationship between Freundlich's constants taken from the literature and molecular refraction

Literature	Freundlich's constant	Number of compounds	a	b	r	s	F	t
Ref. 5	log (k/mg)	14	1.385	−4.981	0.9423	0.5461	95.04	9.749***
	log (k/mol)	14	0.03098	−3.596	0.6609	0.3903	9.305	3.050*
	$1/n$	14	−0.01997	1.240	−0.8507	0.1369	31.42	−5.605***
Ref. 6	log (k/mg)	8	0.08790	−2.535	0.9106	0.4501	29.14	5.399**
	log (k/mol)	8	−0.01669	−1.108	−0.4593	0.3644	1.604	−1.266
	$1/n$	8	−0.01924	1.240	−0.8289	0.1465	13.17	−3.630*

Table 5. Results of multiple-regression analysis for the $\log X = \alpha\Phi + \beta + \gamma \log C$ equation

Φ	α	β	γ	r	s	F	$t(\Phi)$	t (log C)
MR	0.07134	−1.983	0.4401	0.9651	0.1505	1004***	44.48***	13.62***
P	0.009583	−2.359	0.4029	0.9556	0.1692	779.0***	39.17***	11.19***
MW	0.01971	−2.147	0.3749	0.9082	0.2404	384.3***	26.17***	7.323***
CN	0.2785	−1.028	0.4081	0.8936	0.2578	293.3***	24.01***	7.337***

the adsorption isotherms of 14 amino acids on Darco G-60, a commercial-grade lignite carbon. Urano et al.[6] measured the adsorption isotherms of 8 amino acids on two activated carbons from coal and petroleum pitch. Table 4 shows the relationship between Freundlich's constants and the molecular refraction. In the original papers, the k values were expressed in mol/g; therefore, the correlation coefficients between log k and the molecular refraction are very low because of the compounds with a high adsorbability, such as tryptophan, phenylalanine, and tyrosine, indicate a maximum adsorption at fairly low concentrations less than 1 mol/l. However, when the k values are expressed in mg/g, the correlation coefficient becomes high. It can be seen from Table 4 that Eqs. 2 and 3 are also applicable to the other activated carbons.

From Eqs. 1 and 2 we obtain the following equation, with a slight change in notation:

$$\log X = \alpha\Phi + \beta + \gamma \log C, \tag{4}$$

where α, β, and γ are constants. The data of 151 plots of 17 amino acids have been given to a NEC PC-8001 computer in order to determine the α, β, and γ values by means of multiple regression analysis. The constants and statistic analysis for several physical constants are given in Table 5. High correlation coefficients have been obtained for the molecular refraction and the parachor. Figure 4 shows a plot of the log X values observed *vs.* the log X values calculated by means of:

$$\log X_{\text{calcd}} = 0.07134\,MR - 1.983 + 0.4401 \log C. \tag{5}$$

We can see from Fig. 4 that the molecular refraction gives a good prediction of the isotherms.

If the α, β, and γ constants for a given activated carbon are determined from the adsorption data of several compounds, the adsorption isotherms of many other amino acids can be predicted from the molecular refraction alone. It should be remembered, however, that the solution pH influences the adsorption of ionized solutes.[7–9] These prediction methods may not be applicable for adsorptions at pH values extremely removed from the isoelectric point.

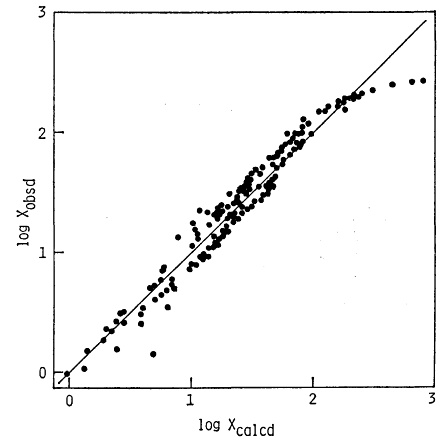

Fig. 4. Relationship between log X observed and log X calculated using Eq. 5.

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