Application of a Group Contribution Method for Predicting Adsorbability on Activated Carbon

S. P. CHITRA and
RAKESH GOVIND

Department of Chemical & Nuclear
Engineering
University of Cincinnati
Cincinnati, OH 45221

INTRODUCTION

Due to the growing concern for potential carcinogenic, mutagenic, and teratogenic compounds found in drinking water, there is a strong need for a method of predicting single-solute isotherms for a wide variety of organic compounds. While numerous experimental studies have been done for several well know toxic chemicals, in many cases no experimental data are available.

In this short paper a new group contribution method has been developed for predicting single-solute isotherms for adsorption on activated carbon. The method is based on the well-known group contribution method, which has been successful in estimating a variety of pure-component properties such as liquid densities, heat capacities, and critical constants.

BACKGROUND

Although adsorption data for activated carbon are limited, Arbuckle and Ramagnoli (1979) concluded that the compound with the higher Freundlich K constant was preferentially adsorbed. Hence the Freundlich K values, if known, could be used to estimate the carbon usage if activated carbon was used for its removal from waste water.

Other models that have been proposed in the literature for predicting relative equilibrium loadings are:

1. Solvophobic theory
2. Polanyi adsorption theory
3. Net adsorption energy theory
4. Theory of correspondence (Myers and Sircar, 1983)

The first three theories have been discussed by Arbuckle (1981). Recently Arbuckle (1983) has compared the four models using the experimental data obtained by Arbuckle and Ramagnoli (1979).

THE GROUP CONTRIBUTION APPROACH

The fundamental assumption of a group contribution method is additivity; the contribution made by a group is assumed to be independent of that made by another group. Application of the group contribution idea to mixtures is attractive because a very large number of multicomponent mixtures of interest can be constituted from perhaps a few hundred functional groups.

If a mixture of solutes in solution is in equilibrium with an adsorbent then,

$$\mu_{i\phi} = \mu_{iB} \tag{1}$$

where the subscripts ϕ and B indicate the adsorbed phase and the bulk phase, respectively. Expressing the chemical potentials in Eq. 1 in terms of mole fraction x_i and activity coefficient γ_i, we get

$$\mu_{i\phi}^o - \mu_{iB}^o = RT\ln\left(\frac{x_{iB}\gamma_{iB}}{x_{i\phi}\gamma_{i\phi}}\right) \tag{2}$$

Assuming that the adsorbed phase is an ideal phase with the activity coefficient $\gamma_{i\phi} = 1$, and the liquid phase is an ideal dilute solution and hence $\gamma_{iB} = 1$, then Eq. 2 becomes

$$\mu_{i\phi}^o - \mu_{iB}^o = RT\ln\left(\frac{x_{iB}}{x_{i\phi}}\right) \tag{3}$$

Defining the adsorption potential of a solute i from aqueous solution as

$$\epsilon_i = \mu_{iB}^o - \mu_{i\phi}^o \tag{4}$$

Eq. 3 can be written as

$$\frac{\epsilon_i}{RT} = \ln\left(\frac{x_{i\phi}}{x_{iB}}\right) \tag{5}$$

Since the group solution model will be used to predict adsorption potentials of organic compounds in aqueous solution, we define

$$\frac{\epsilon_i}{RT} = \beta_i \ln x_{iB} \tag{6}$$

Combining Eqs. 5 and 6 we get

$$\ln\left(\frac{x_{i\phi}}{x_{iB}}\right) = \beta_i \ln x_{iB} \tag{7}$$

This equation is similar to the Freundlich isotherm equation, when written in terms of bulk concentration C_B (mmol/L) and

---

Correspondence concerning this paper should be addressed to Rakesh Govind.

TABLE 1. GROUP CONTRIBUTION α_k CONSTANTS a_O AND B IN THE MODEL

Group	Formula	Constant	95% Confidence Limits d.f. = 293
Methylene	$-CH_3$	−0.77827	±0.01172
Ethylene	$-CH_2$	−0.18510	±0.01097
Acetylene	CH	0.43332	±0.05889
Aldehyde	CHO	0.44027	±0.01639
Acetate	COO	0.91498	±0.00004
Ketone	CO	1.07622	±0.01141
Hydroxyl	OH	0.64353	±0.02808
	B	0.01177	±0.00106
	a_o	0.18682	±0.19420

adsorbability Y (mmol compound/g adsorbate). Equation 7 can be written as

$$\ln\left(\frac{Y_i}{C_{Bi}}\right) + \ln C_1 = \beta_i \ln(C_{Bi}) + \beta_i \ln C_2 \tag{8}$$

By comparing with the Freundlich isotherm equation, the following equations can be obtained

$$K = (C_2)^{\beta_i}/C_1 \tag{9}$$

$$\frac{1}{n} = 1 + \beta_i \tag{10}$$

Where C_1 and C_2 are conversion factors from mole fraction to the appropriate units of Y and C_{Bi}.

From the group contribution, β_i depends on the functional groups present and their concentration, and on the size and concentration of the ith molecule. Hence β_i can be decomposed into size or structural contribution (β_i^S) and group contribution, β_i^G, or

$$\beta_i = \beta_i^G + \beta_i^S \tag{11}$$

Following the work of Manipuri and Ratcliff (1971) we take

$$\beta_i^S = B\left(N_i - \sum_j x_j N_j\right)^2 \tag{12}$$

This is a generalization of the theory of congruence and has been successfully used for predicting excess free energies for mixtures (Maripuri and Ratcliff, 1971). Values for the constant B are obtained from experimental data.

The group contributions, β_i^G, is assumed to be the sum of the individual contributions of each group present and is expressed in terms of the contribution ϕ_k for individual groups

$$\beta_i^G = \sum_k N_{ki}(\phi_k - \phi_k^*) \tag{13}$$

The individual group contribution, ϕ_k, depends on composition and temperature

$$\phi_k = \phi_k(X_1, X_2, \ldots T) \tag{14}$$

where X_i = group fraction defined as follows

$$X_i = \frac{\sum_i x_k N_{ki}}{\sum_k \sum_i x_i N_{ki}} \tag{15}$$

TABLE 2. ESTIMATED FREUNDLICH CONSTANTS FROM THE GROUP CONTRIBUTION MODEL

Compound	Actual K	Est. K	Actual $1/n$	Est. $1/n$
1-propanol	0.130	0.1410	0.730	0.602
2-methyl-1-propanol	0.310	0.3296	0.588	0.523
1-pentanol	1.180	1.0315	0.508	0.420
2-ethyl-1-hexanol	2.610	2.24133	0.263	0.348
Ethyl acetate	0.510	0.6074	0.549	0.467
Butyl acetate	1.46	1.5839	0.826	0.380
Butyraldehyde	0.490	0.5296	0.628	0.481
Acetone	0.110	0.1080	0.599	0.625
Methyl ethyl ketone	0.350	0.3319	0.546	0.523
Methyl isobutyl ketone	1.12	1.0984	0.332	0.413
Ethyl butyl ketone	2.14	2.0555	0.275	0.356

$K\ \Sigma\ (\text{Error})^2 = 0.1928$ $1/n\ \Sigma\ (\text{Error})^2 = 0.2772$

In adsorption from water the concentration of the chemical is usually very small (mole fraction of the order of 10^{-6}) and hence the difference ($\phi_k - \phi_k^*$) can be considered to be independent of composition and Eq. 13 can be written as

$$\beta_i^G = \sum_k N_{ki}\alpha_k \tag{16}$$

Combining Eqs. 7, 11, 12, 13, and 16 with allowance for regression error (a_o) we get

$$\ln(x_{i\phi}/x_{iB}) = a_o + \sum_k N_{ki}\alpha_k \ln x_{iB} + B\left(N_i - \sum_j N_j x_j\right)^2 \ln x_{iB} \tag{17}$$

where a_o is the regression intercept and for a perfect fit a_o approaches zero.

MODEL VERIFICATION

The above model is verified by using the available adsorption isotherms (Arbuckle, 1981) to obtain the constants α_k, B, and a_o in Eq. 17. The available isotherms for 2-propanol, 1-butanol, 2-hexanol, 2-ethyl-1-butanol, propionaldehyde, butyl acetate, and diethyl ketone were used to compute all the group contributions, α_k, and constants B and a_o, as given in Table 1. The concentration range used in estimation is 0.3–2.7 mmol/L. A multiple regression program is used to obtain the nine model parameters using the isotherm data (Draper and Smith, 1966).

The group contributions (α_k) are then used for predicting the Freundlich isotherm parameters (K and n) for other compounds not used in the regression analysis. Using Eqs. 9 and 10, Freundlich isotherm parameters are calculated. Since the group contributions (α_k) in Table 1 are estimated for the concentration range of 0.3–2.7 mmol/L, the predicted values summarized in Table 2 are also applicable for the same concentration range.

RESULTS AND DISCUSSION

As can be seen from Table 2 the reported results agree quite well with the predicted values. It should be noted that the group contributions α_k and the constants B and a_o were obtained from the Freundlich isotherms since the actual experimental data were not available. Since the Freundlich isotherms were obtained by regression analysis there was some error in the data used for our estimations (for example, the n value for butyl acetate).

The group contributions α_k and the constants B and a_o can be used to estimate the adsorption isotherm for any organic compound that consists of the groups listed in Table 1. Hence the results are more generally applicable than the Freundlich isotherm constants, which have to be determined for each compound.

Finally it should be noted that the group contribution procedure is restricted to the type of activated carbon used for estimating the group contributions α_k and the constants B and a_o. Variations with respect to the type of activated carbon have not been addressed in this paper. Further, the isotherm concentration range in which this technique is applicable depends on the assumptions that the liquid phase is an ideal dilute solution and that the difference $(\phi_k - \phi_k^*)$ is independent of composition.

ACKNOWLEDGMENT

This research was supported by a contract from the Environmental Protection Agency.

NOTATION

a_o = constant in Eq. 17
B = constant in Eq. 12
C_{Bi} = concentration of the ith solute in solution, mmol/L
C_1C_2 = constants in Eq. 9
K = Freundlich equation parameter
n = Freundlich equation parameter
N_j = number of atoms other than hydrogen in molecule j
N_{ki} = number of groups of type k in molecule i
R = gas constant
T = temperature
X = group fraction
x = mole fraction
Y = adsorbability of carbon, mmol solute/g carbon

Greek Letters

α = defined as $(\phi - \phi^*)$ for each group
β = group dependent parameter
μ = chemical potential
γ = activity coefficient
ϵ = adsorption potential
ϕ = contribution of each group

Subscripts

B = bulk phase
i = molecular species i
j = molecular species j
k = group species k
ϕ = adsorbed phase

Superscripts

$o,*$ = standard state
G = group contribution
S = structural contribution

LITERATURE CITED

Arbuckle, W. B., "Estimating Equilibrium Adsorption of Organic Compounds on Activated Carbon from Aqueous Solution," *Env. Sci. Tech.*, **15**, 812 (1981).

———, "Comparison of Granular Activated Carbon Equilibria Models," private communication (1983).

Arbuckle, W. B., and R. J. Romagnoli, "Prediction of the Preferentially Adsorbed Compound in Bisolute Studies," *Water—1979, Chem. Eng. Prog. Symp. Ser.*, **76**, 77 (1980).

Draper, N. R. and H. Smith, *Applied Regression Analysis*, Wiley, New York (1966).

Maripuri, V. C., and G. A. Ratcliff, "Prediction of Excess Free Energies by a Group Solution Model with Application to Alkane/Ketone Mixtures," *Can. J. Chem. Eng.*, **49**, 375 (1971).

Myers, A. L. and S. Sircor, "Theory of Correspondence for Absorption from Dilute Solutions on Heterogeneous Adsorbents", *Treatment of Water by Granular Activated Carbon*, M. J. McGuire and I. H. Suffet, eds., *Adv. in Chem. Ser.*, **202**, 63, ACS, Washington, DC (1983).

Manuscript received Feb. 29, 1984, and revision received Dec. 17, 1984.