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Simultaneous Determination of Multi-Component Isotherm Parameters from Single Sample of Liquid

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Abstract. For the adsorption of multiple organic compounds using activated carbon in aqueous systems, several useful models have been developed to describe the equilibrium relationship. One of the easy-to-use models was developed by Suzuki et al. and the model was extended to determine equilibrium parameters for each component simultaneously. The determination procedure required liquid mixtures at various initial concentrations. The industrial sample, however, is normally controlled at constant concentration and hence the determination procedure mentioned above was limited to be applied. In this study, simultaneous determination procedure of multi-component isotherm parameters from single sample was discussed theoretically and experimentally. Then, it was found that Freundlich-type parameters for each component dissolved in water could be obtained from constant composition solutions based on Ideal Adsorbed Solution Theory.

Keywords: multi-component, IAS theory, Freundlich equation, parameter determination

1. Introduction

For the design of an adsorption process, kinetic and adsorptive equilibrium parameters are required. For the adsorption of multiple organic compounds using activated carbon in aqueous systems, several useful models have been developed to describe the equilibrium. Myers and Prausnits presented the Ideal Adsorbed Solution (IAS) theory for gaseous phase multi-component adsorption (Myers et al., 1965). Radke and Prausnitz later extended the IAS theory to dilute liquid solutions (Radke et al., 1972). Suzuki applied Freundlich isotherm in IAS theory and developed easy-to-use equations for the estimation of multi-component equilibrium (Suzuki et al., 1983). Finally, Furuya extended Suzuki's model and developed a technique to determine the isotherm parameters from multi-component aqueous samples (Furuya et al., 1986).

In the previous laboratory study, Furuya et al. varied the initial concentration of adsorbates in a multi-component system to determine the isotherm parameters. However, liquid samples from industrial processes normally only have a set of, if not fixed, concentrations for a given process stream. In other words,

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the composition of a process stream is normally controlled at a constant level for reproducibility. Furthermore, pure compounds are often not isolated and become available for the preparation of a varying composition. As a result, the previous study has limited application.

In this study, a technique for the simultaneous determination of multi-component Freundlich isotherm parameters in an aqueous system was developed using test data from a single sample composition. The technique was first derived theoretically and then verified experimentally.

2. Fundamental Equations

Equations (1) to (3) were derived by use of assumptions of (a) adsorbent solid is inert, (b) molecular sieving effect is negligible, (c) chemical potentials of adsorbed and liquid phases are identical, (d) effect of pressure on liquid phase properties is negligible, (e) adsorption of each component obeyed Freundlich isotherm, and (f) multi-component adsorption can be described by ideal adsorbed (IAS) solution [7] concept.

$$\Pi = \frac{\pi A}{RT} = \int_0^{c_i^0} \left(\frac{q_i^o}{c_i^0}\right) dc_i^0 \tag{1}$$

$$\frac{1}{q_t} = \sum \left(\frac{Z_j}{q_j^0}\right) \tag{2}$$

$$Z_i = \left(\frac{q_i}{q_t}\right) \tag{3}$$

$$q_t = \sum q_j \tag{4}$$

where A denotes specific internal surface area of adsorbent, c_i is liquid phase concentration of solute i, and q_i is amount adsorbed of component i. R means gas constant and T is absolute temperature. π denotes spreading pressure and superscript 0 means a value for single component adsorption at the same spreading pressure and the same temperature as those for multi-component systems.

By substituting the Freundlich-type equations ($q_i^0 = k_i(c_i^0)^{1/n_i}$) to the adsorption equilibria, Eq. (1) is integrated to give [2, 8]:

$$\Pi = n_i k_i \left(c_i^0\right)^{1/n_i} \tag{5}$$

where dimensionless variables employed here were;

$$c_i^0 = \left(\frac{\Pi}{n_i k_i}\right)^{n_i} \tag{6}$$

$$q_i^0 = \frac{\Pi}{n_i} \tag{7}$$

$$\Pi = \sum n_j q_j \tag{8}$$

On the other hand, the following equation can be obtained from Eq. (3).

$$c_i^0 = \left(\frac{c_i}{q_i}\right) q_t \tag{9}$$

Equations (5) and (6) provide a ratio of c_i^0 to c_j^0 as follows:

$$\begin{aligned}\left(\frac{c_i^0}{c_j^0}\right) &= \left(\frac{\Pi}{n_i k_i}\right)^{n_i} \Big/ \left(\frac{\Pi}{n_j k_j}\right)^{n_j} \\ &= \left(c_i^0\right)^{\{1-(n_j/n_i)\}} \left(\frac{n_j k_j}{n_i k_i}\right)^{n_j}\end{aligned} \tag{10}$$

Therefore, one can obtain the value of n_j/n_i from slope by plotting (c_i^0/c_j^0) as a function of c_i^0 on a logarithmic graph, provided that k_i, k_j, n_i, and n_j are constant.

As to the calculation of q_i^0, Eq. (11) can be derived by substituting the right-hand-side of Eq. (8) for Π on Eq. (7).

$$q_i^0 = \sum_j \left(\frac{n_j}{n_i}\right) q_j \tag{11}$$

Therefore, the adsorption equilibrium for single component system, c_i^0 and q_i^0, can be estimated from the equilibria for multi-component system as follows:

(a) Values of c_i^0 and c_i^0/c_j^0 are estimated from Eqs. (9) and (12), respectively, using the values of c_i, c_j, q_i, and q_j.

$$\left(\frac{c_i^0}{c_j^0}\right) = \left(\frac{c_i}{c_j}\right) \Big/ \left(\frac{q_i}{q_j}\right) \tag{12}$$

(b) Values of (n_j/n_i) is calculated from the plot of $\log(c_i^0/c_j^0)$ against $\log(c_i^0)$.

(c) The adsorption equilibrium for respective single component systems can be estimated by use of Eq. (11) and the value of (n_j/n_i).

3. Computational Approach

Base on the IAS theory, liquid phase concentration for each component dissolved in water mixture can be estimated from amount adsorbed for all solutes as follows:

(a) Estimate Π by use of Eq. (8) with amounts adsorbed and Freundlich parameters.
(b) Evaluate the value of c_i^0 for each component.
(c) Calculate liquid concentration for each component by Eq. (9).

The procedure mentioned above can be formulated as;

$$c_i = \left(\frac{q_i}{q_t}\right)c_i^0 = \left(\frac{q_i}{q_t}\right)\left(\frac{\Pi}{n_i k_i}\right)^{n_i} = \left(\frac{q_i}{q_t}\right)\left(\frac{\sum n_j q_j}{n_i k_i}\right)^{n_i} \tag{13}$$

For multi-component batch adsorption, on the other hand, liquid phase concentration c_i in equilibrium with amounts adsorbed, q_i, for component i $(i = 1 \sim n)$ can be obtained as;

$$c_i = c_{0,i} - \left(\frac{m}{V}\right)q_i \tag{14}$$

Combining Eqs. (13) and (14), amounts adsorbed, q_i, can be determined easily for given values of $c_{0,i}$, m, V, and Freudlich parameters, k_i and n_i, with the aids of "solver in the excel".

4. Results and Discussions

4.1. Experimental Approach

The analysis technique mentioned above was tested by the following method. Simulated wastewater samples employed for preliminary research were composed of two aromatic compounds. The initial concentration ratio for each run was different each other.

For phenol—benzoic acid system, the amount adsorbed of each component, was estimated from experimental values for binary system by the batch bottle technique described above. For each run, Values of adsorbate concentration for single component adsorption at the same T and p as those for multi-component system, c_i^0, were estimated by Eq. (9) and also values of (n_i/n_j) were calculated. In the Fig. 1, relationship between c_2^0 and (c_2^0/c_1^0) were illustrated. From the linear regression line shown in the figure, value of n_1/n_2 was determined to be 0.6877.

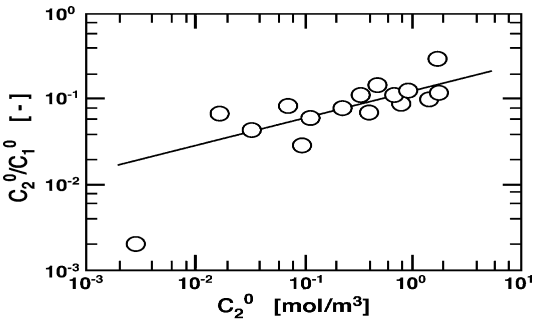


Figure 1. Determination of (n_1/n_2) value for phenol—benzoic acid system.

The adsorption equilibrium for respective single component systems was estimated by use of Eq. (11) with the value (n_1/n_2). For single component systems, adsorption equilibria were also obtained experimentally by using the batch bottle technique. These results for both single and binary adsorption systems are shown in Fig. 2(a) and (b).

The points clarified from the figures are summarized as "Adsorption isotherms for each component estimated by the procedure agreed well with those measured experimentally for single component adsorption".

4.2. Numerical Approach

As mentioned above, simulated multi-component adsorption equilibria can be easily generated by combining Eqs. (13) and (14) for given values of $c_{0,i}$, m, V, and Freudlich parameters, k_i and n_i, with the aids of "solver in the excel". In this study, simulated adsorption equilibrium was calculated by the procedure with values summarized in Table 1. The Freundlich parameters employed here were similar to those for aromatic compound—activated carbon systems.

Solid and fluid concentration data at equilibrium, q_e and c_e, are obtained by using three different initial concentrations (the concentration ratio was unchanged) and three solid/liquid ratios as 20.0, 16.0 and 12.0. From thus-obtained data, equilibrium concentrations were scattered except two values and hence the determination procedure seemed to be applicable.

Table 1. Original concentrations and equilibrium parameters employed for case 1.

	Component 1	Component 2	Component 3
c_0 (mg/L)	600	600	600
M (g/mol)	60.1	74.1	88.2
c_0 (mol/L)	9.98	8.10	6.80
n	2.10	2.57	2.65
k (mol/g)	0.12	0.40	0.80

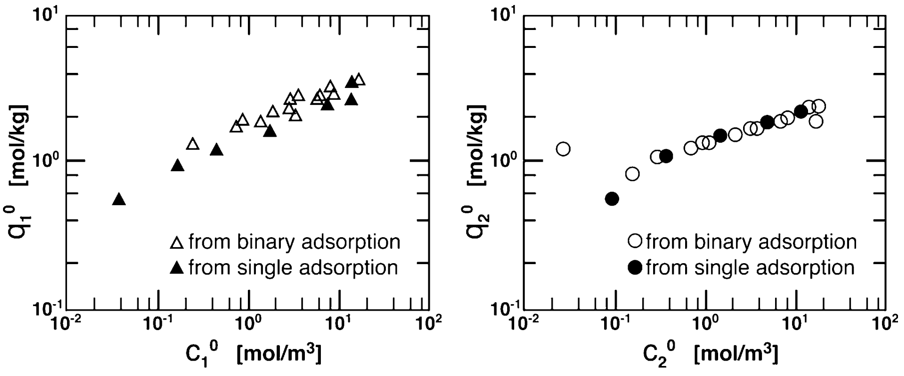
As mentioned in experimental approach section, values of (c_i^0) and (c_i^0/c_j^0) for each run were calculated and values of $\log(c_i^0)$ were plotted against $\log(c_i^0/c_j^0)$. While 9 simulated data were generated, only 8 points were shown in figures. This means that two points were obtained as almost the same value.

From the relationship between c_1^0 of component 1 and (c_1^0/c_2^0), a value of (n_2/n_1) was obtained as 1.224_6 by use of the calculation procedure mentioned above.

Table 2. Equilibrium parameters obtained from Fig. 4.

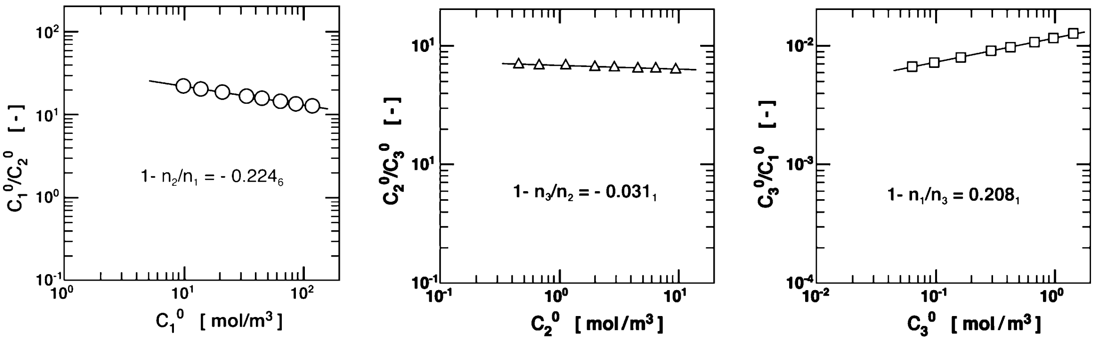
	Component 1	Component 2	Component 3
n	2.09_9	2.57_0	2.64_9
k (mol/g)	0.11_9	0.39_9	0.79_9

From plots of (c_2^0/c_3^0) against c_2^0 of component 2 and (c_3^0/c_1^0) against c_3^0 of component 3, values of (n_3/n_2) and (n_1/n_3) were determined as 1.031_1 and 0.791_9, respectively. Then, all values of c_i^0 and q_i^0 for each run were determined from equilibrium data, i.e. (c_1, q_1), (c_2, q_2) and (c_3, q_3) by use of Eqs. (9) and (11). The results estimated for each component are shown in Fig. 4. For the estimation of all (n_i/n_j) values from the data, only two figures are required, while three figures can be illustrated from thus-generated equilibrium relationships. Freundlich parameters were determined from intercept and slope of regression line within each figure in Fig. 4 and the obtained values were summarized in



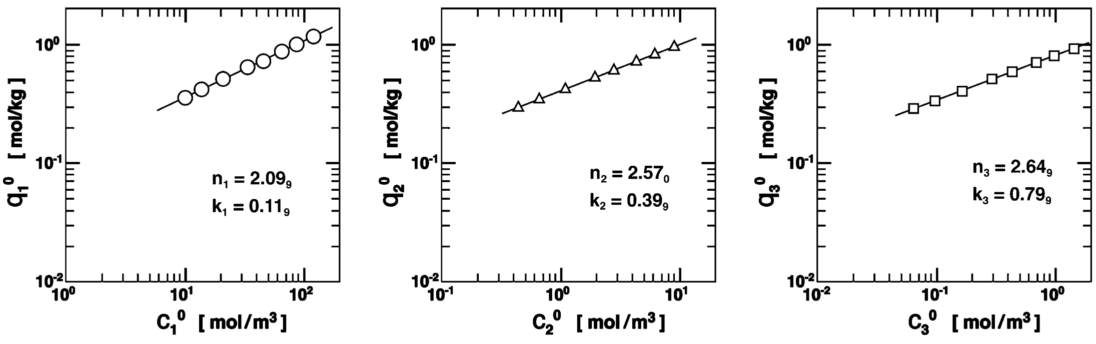
(a) Phenol (b) Benzoic acid

Figure 2. Adsorption isotherm determined from single and binary adsorption.



(a) n_2/n_1 (b) n_3/n_2 (c) n_1/n_3

Figure 3. Determination of (n_i/n_j) value for ternary component system.



(a) Component 1 (b) Component 2 (c) Component 3

Figure 4. Adsorption isotherm determined from ternary adsorption.

Table 2. These values are very close to those shown in Table 1.

5. Conclusions

A technique for the simultaneous determination of multi-component Freundlich isotherm parameters in an aqueous system was developed using test data from a single sample composition. The technique was derived theoretically and experimentally.

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