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The *Langmuir-Freundlich* Equation in Adsorption from Dilute Solutions on Solids

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Correlation between parameters obtained from the signle-solute and bi-solute adsorption data by means of the *Langmuir-Freundlich* equation has been studied.

(Keywords: Adsorption from dilute solutions; Langmuir-Freundlich isotherm equation; Correlation between single-solute and bi-solute adsorption parameters)

Die Langmuir-Freundlich-Gleichung in der Adsorption von verdünnten Lösungen an Festkörpern

Die Korrelation zwischen den bei Anwendung der *Langmuir-Freundlich*-Gleichung erhaltenen Adsorptionsparametern für Einzel- und Binärkomponentenlösungen wurde untersucht.

Introduction

Theoretical studies of multi-solute adsorption from dilute solutions on energetically heterogeneous solids have been presented in the earlier papers[1–9]. It follows from these studies that the isotherm equations corresponding to quasi-*Gaussian* energy distribution give the best agreement with the experimental data[1,5,6]. One of these equations, frequently used in gas[10,11] and liquid adsorption[12,13], may be written as follows[6]:

$$\theta_i^0(c_i) = \frac{(K_i c_i)^{m_i}}{1 + (K_i c_i)^{m_i}} \tag{1}$$

where θ_i^0 and c_i are the relative single-solute adsorption and concentration of the i-th solute, respectively, K_i is the *Langmuir*-type constant determining position of the energy distribution on the energy

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axis, and m_i is the heterogeneity parameter connected with the width of this distribution. Equation (1), called the *Langmuir-Freundlich* isotherm, describes the monolayer single-solute adsorption from dilute solutions on heterogeneous solid surfaces showing quasi-*Gaussian* distribution of adsorption energies. This equation has been extended to multi-solute adsorption[6] by using two different approximations, analogous to those used in adsorption of gas[14,15] and liquid mixtures[16,17]. The extended forms of Eq. (1), describing the multi-solute adsorption, may be expressed as follows[6]:

$$\theta = \frac{\sum_{i=1}^{n} (K_i c_i)^m}{1 + \sum_{i=1}^{n} (K_i c_i)^m} \tag{2}$$

and

$$\theta = \frac{(K_1 y)^{m_1}}{1 + (K_1 y)^{m_1}} \tag{3}$$

where

$$y = c_1 + \sum_{i=2}^{n} (K_i/K_1) c_i \tag{4}$$

In the above θ is the total relative adsorption of n solutes from a dilute solution, and m is the heterogeneity parameter characteristic for a given adsorption system.

Results and Discussion

In this communication, we will discuss the correlation between values of m_i obtained from the single-solute and bi-solute adsorption data by means of Eqs. (1), (2) and (3). The experimental data for single-solute and bi-solute adsorption from dilute aqueous solutions on activated carbon, measured by *Fritz*[18] and discussed by *Digiano* et al.[3], were used to study this correlation. The parameters a_{mi}, K_i and m_i for single-solute adsorption data, where a_{mi} is the maximum adsorption of the solute in the monolayer and θ_i^0 is defined as the ratio of the solute adsorbed amount to a_{mi}, were evaluated by using the linear form of Eq. (1):

$$\ln [\theta_i^0/(1-\theta_i^0)] = m_i \ln K_i + m_i \ln c_i \tag{5}$$

These parameters are summarized in Table 1. Next, the bi-solute adsorption data were approximated by the linear forms of Eqs. (2) and (3) for $n = 2$:

$$\ln(\theta_1/\theta_2) = m \ln K_{12} + m \ln(c_1/c_2) \tag{6}$$

$$\ln[\theta/(1-\theta)] = m_1 \ln K_1 + m_1 \ln(c_1 + K_{21} c_2) \tag{7}$$

where

$$K_{12} = K_1/K_2;\ K_{21} = (K_{12})^{-1} \tag{8}$$

$$\theta = \sum_{i=1}^{n} \theta_i \tag{9}$$

and θ_i is the partial relative adsorption of the i-th solute. The bi-solute adsorption data of *Fritz*[18] were analysed by means of the linear relationship (6) by *Deryło* and *Jaroniec*[6]. However, the parameters a_m, K_1, K_{21} and m_1 of Eq. (7) obtained for these data, are summarized in Table 2. Fig. 1 presents the linear plots $\ln[\theta/(1-\theta)]$ vs. $\ln(c_1 + K_{21} c_2)$

Table 1. *Parameters a_{mi}, K_i and m_i of Eq. (5), characterizing the single-solute adsorption from dilute aqueous solutions on activated carbon at 293 K*

Solute	a_{mi} [mmol/g]	K_i	m_i
phenol	7.0	0.12	0.38
p-nitrophenol	5.9	2.26	0.28
p-chlorophenol	5.3	2.74	0.34
benzoic acid	6.0	1.17	0.41

Table 2. *The parameters of Eqs. (5), (6) and (7) characterizing the single-solute and bi-solute adsorption from dilute aqueous solutions on activated carbon at 293 K*

Solute "1"	Solute "2"	a_m [mmol/g]	K_{21}	K_1 [Eq. 7]	K_1 [Eq. 5]	m_1 [Eq. 7]	m_1 [Eq. 5]	m [Eq. 6]
phenol[a]	*p*-nitrophenol	6.45	18.8	0.15	0.12	0.33	0.38	0.70
phenol[b]	*p*-nitrophenol	6.45	18.8	0.08	0.12	0.29	0.38	0.76
p-nitrophenol	*p*-chlorophenol	5.6	1.2	2.42	2.26	0.34	0.28	0.90
p-nitrophenol	benzoic acid	5.95	0.52	2.6	2.26	0.35	0.28	0.90

[a] Parameters characterizing adsorption from low concentration range.

[b] Parameters characterizing adsorption from high concentration range.

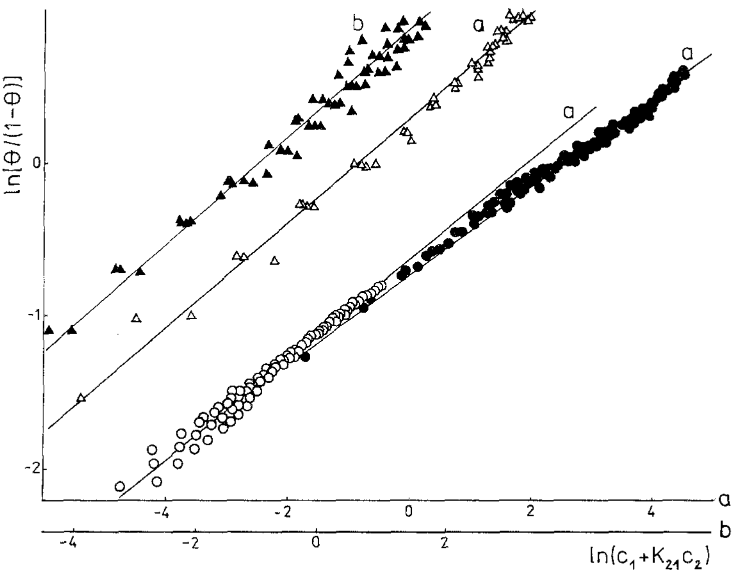

Fig. 1. The linear dependence $\ln[\theta/(1-\theta)]$ vs. $\ln(c_1 + K_{21} c_2)$ for adsorption of: phenol(1) + *p*-nitrophenol(2) (low concentration range) (○); phenol(1) + *p*-nitrophenol(2) (high concentration range) (●); *p*-nitrophenol(1) + *p*-chlorophenol(2) (Δ); *p*-nitrophenol(1) + benzoic acid (2) (▲) from dilute aqueous solutions on activated carbon at 293 K

for bi-solute adsorption systems. It follows from Fig. 1 that Eq. (7), similarly as the relationship (6), gives a good representation of the experimental data. Moreover, the parameters K_1 obtained from single-solute data by means of Eq. (5) and from bi-solute data by means of Eq. (7) are similar. The values of m obtained by means of Eqs. (5), (6) and (7) are also compared in Table 2. It follows from this comparison that the values of m obtained by means of Eqs. (5) and (7) are similar. It means that the bi-solute adsorption data may be predicted by means of Eq. (7) using the single-solute adsorption parameters of Eq. (5). The other important conclusion concerns the theoretical dependence between Eqs. (5), (6) and (7). A good correlation between the parameters of Eqs. (5) and (7) means that only Eq. (7) may be considered as an extension of Eq. (5). However, the similarity between Eqs. (5) and (6) has a formal character only; the single-solute adsorption parameters of Eq. (5) are not suitable for predicting the bi-solute adsorption data by means of Eq. (6).

References

[1] *Jossens L., Prausnitz J. M., Fritz W., Schlünder E. U., Myers A. L.*, Chem. Eng. Sci. **33**, 1097 (1978).

[2] *Sheindorf Ch., Rebhum M., Sheintuch M.*, J. Colloid Interface Sci. **79**, 136 (1981).

[3] *Digiano F. A., Baldauf G., Frick B., Sontheimer H.*, Chem. Eng. Sci. **33**, 1667 (1978).

[4] *Okazaki M., Kage H., Jijia F., Toei R.*, J. Chem. Eng. Japan **14**, 26 (1981).

[5] *Jaroniec M., Deryło A.*, J. Colloid Interface Sci. **84**, 191 (1981).

[6] *Deryło A., Jaroniec M.*, Chemica Scripta **19**, 108 (1982).

[7] *Jaroniec M., Deryło A.*, in: Physicochemical Methods in Water and Wastewater Treatment (*Pawłowski L.*, ed.), p. 361. Amsterdam: Elsevier. 1982.

[8] *Jaroniec M.*, J. Colloid Interface Sci. **86**, 588 (1982).

[9] *Jaroniec M., Deryło A.*, Chem. Eng. Sci. **36**, 1917 (1981).

[10] *Sips J. R.*, J. Chem. Phys. **16**, 420 (1948).

[11] *Crickmore P. J., Wojciechowski B. W.*, J. Chem. Soc. Faraday I **73**, 1216 (1977).

[12] *Dąbrowski A., Ościk J., Jaroniec M., Rudziński W.*, J. Colloid Interface Sci. **69**, 287 (1979).

[13] *Dąbrowski A., Jaroniec M.*, J. Colloid Interface Sci. **73**, 475 (1980).

[14] *Jaroniec M.*, J. Res. Inst. Catalysis (Hokkaido Univ.) **28**, 31 (1980).

[15] *Jaroniec M.*, Thin Solid Films **71**, 273 (1980).

[16] *Jaroniec M.*, J. Res. Inst. Catalysis (Hokkaido Univ.) **26**, 155 (1978).

[17] *Jaroniec M., Ościk J., Deryło A.*, Acta Chim. Acad. Sci. Hung. **106**, 257 (1981).

[18] *Fritz W.*, Dissertation, Universität Karlsruhe, FRG 1978.