MULTICOMPONENT ADSORPTION EQUILIBRIA OF PHENOLS ON ACTIVATED CARBON

Application of Ideal Adsorbed Solution (IAS) Theory

Hee Joon Kim, Hee Moon and Heung Chul Park*

Department of Chemical Process, Chonnam National University
Kwangju, Chonnam 505, Korea

(Received 21 May 1985 • accepted 25 July 1985)

Abstract — Multicomponent adsorption equilibria of phenols on activated carbon were predicted by the ideal adsorbed solution (IAS) theory and results were compared with those calculated from two different Freundlich-type isotherms. Although some deviations between measured and calculated results are observed, the IAS theory permits rapid and relatively accurate predictions of adsorption equilibria for two-and three-component systems comparing with other isotherms. The results obtained show that the IAS theory is quite suitable for the extended application to multicomponent adsorption systems.

INTRODUCTION

Adsorption onto activated carbon has been known as a useful and effective method for the removal of toxic compounds in waste waters. The prediction of adsorption equilibria is quite necessary for the understanding of adsorption phenomena and for the incorporation into kinetic models. To find a proper multicomponent equilibrium relation, however, is not simple since industrial and municipal wastes contain a vast number of organic substances and a thorough understanding of the interaction between components is lacking. Keith and Telliard [1] reported 129 priority pollutants, which must be removed from waste waters. Thus, the equilibrium relation must be of a form that can be easily applied to multicomponent adsorption systems.

During the past decade, the relations for representation of multicomponent adsorption equilibria have been reported. Jain and Snoeyink [2] proposed a modified version of Langmuir isotherm under the hypothesis that a certain amount of adsorption occurs without competition. But, the relation based on the Langmuir's theory is not likely to give accurate predictions of adsorption equilibria on highly heterogeneous adsorbents. In most cases, the Freundlich type isotherm is suitable for liquid phase adsorption on activated carbons. Fritz and Schlünder [3] proposed a Freundlich-type isotherm for multicomponent systems and this isotherm gives quite accurate predictions. However, its generality remains questionable because many empirical parameters must be determined from single and multicomponent equilibrium data correlations. Another Freundlich type isotherm was derived by Sheindorf et al. [4]. They extended the Freundlich isotherm into multicomponent systems by introducing the competitive coefficient. This coefficient may be determined from two-component data correlations. Since the Sheindorf's isotherm has only an inter-related parameter for each set of two components, it can be applied more conveniently to multicomponent adsorption than the Fritz-Schlünder's isotherm.

In this study, we concentrate on the application of the IAS theory. This theory was first derived by Myers and Prausnitz [5] to predict the adsorption of gases on solids and extended by Radke and Prausnitz [6] to the liquid phase adsorption from dilute solutions. The great advantage of the IAS theory is that it requires only single component equilibrium data in predicting multicomponent equilibria. A simpler method than the IAS theory was derived by Digiano et al. [7]. Although the results calculated by this method are in good agreement with those of the IAS theory in lower concentrations, they diverge at higher concentrations. At present, the IAS theory remains the most viable method of predicting multicomponent equilibria.

IAS THEORY AND MULTICOMPONENT ISOTHERMS

In derivation of the IAS theory, the adsorbent is

---

* To whom all correspondence should be directed.

assumed to be inert and to have a specific surface area identical for all adsorbates. It is also assumed that the adsorbed adsorbates form an ideal adsorbed solution on the surface. In this theory, the spreading pressure of component *i* is represented as follows:

$$\pi_i = \frac{RT}{A} \int_0^{c_i^\circ} Q_i^\circ / C_i^\circ \, dC_i^\circ \qquad (1)$$

Here, π_i is defined as the difference between the interfacial tension of the pure solvent-adsorbent interface and that of the solution-adsorbent interface. The superscript ° denotes single component state. From the definitions of fugacity and chemical potential, the following equations for the IAS theory can be derived:

$$C_i = C_i^\circ(\pi_i, T) \; z_i \qquad (2)$$

$$Q_t = 1/(\sum_{i=1}^{N} z_i/Q_i^\circ) \qquad (3)$$

$$z_i = Q_i/Q_t \qquad (4)$$

$$\sum_{i=1}^{N} z_i = 1 \qquad (5)$$

where z_i is the adsorbed mole fraction of component *i* and Q_t denotes the total number of moles adsorbed. According to the assumption of an ideal adsorbed solution, the spreading pressure of each component must be equal.

$$\pi_1 = \pi_2 = \cdots\cdots\cdots = \pi_N \qquad (6)$$

The most difficult thing in applying the IAS theory arises in the calculation of the spreading pressure from Eq. (1). This can be calculated by analytical or numerical integration according to the form of single component isotherms. Fritz and Schlunder [8] propsed a very simple method for the calculation of π_i using a piecewise Freundlich isotherm as a single component isotherm.

$$Q_i^\circ = A_{i,k} (C_i^\circ)^{p_{i,k}} \qquad (7)$$

where $A_{i,k}$ and $P_{i,k}$ are the Freundlich isotherm parameters for the concentration range of $C_{i,k-l}^\circ \leq C_i^\circ < C_{i,k}^\circ$. $C_{i,k}^\circ$ is the maximum concentration of the k-th range which can be evaluated by matching the k-th and (k+1)-th equations.

Substituting Eq. (7) into Eq. (1), the spreading pressure becomes:

$$\Pi = \frac{1}{p_{i,k}} A_{i,k} (C_i^\circ)^{p_{i,k}} - \delta_{i,k} = \pi_i A/RT \qquad (8)$$

where

$$\delta_{i,k} = \frac{1}{p_{i,k}} A_{i,k} (C_{i,k-1}^\circ)^{p_{i,k}} - \sum_{m=1}^{k-1} \frac{1}{p_{i,m}} A_{i,m} \{(C_{i,m}^\circ)^{p_{i,m}} - (C_{i,m-1}^\circ)^{p_{i,m}}\} \qquad (9)$$

The adsorbed phase concentration, Q_i, can be obtained from Eqs. (3), (4) and (8).

$$Q_i = \{\sum_{j=1}^{N} \frac{z_j}{p_{j,k}(\Pi + \delta_{j,k})}\}^{-1} z_i \qquad (10)$$

The bulk concentration, C_i, which is in equilibrium with Q_i becomes:

$$C_i = \{\frac{p_{i,k}(\Pi + \delta_{i,k})}{A_{i,k}}\}^{(1/p_{i,k})} z_i \qquad (11)$$

Substituting Eq. (11) into Eq. (5) yields

$$\sum_{i=1}^{N} [C_i / \{\frac{p_{i,k}(\Pi + \delta_{i,k})}{A_{i,k}}\}^{(1/p_{i,k})}] = 1 \qquad (12)$$

To calculate Π, Eq. (12) may be rearranged into the following form:

$$F(\Pi) = \sum_{i=1}^{N} [C_i / \{\frac{p_{i,k}(\Pi + \delta_{i,k})}{A_{i,k}}\}^{(1/p_{i,k})}] - 1 = 0 \qquad (13)$$

Newton's iterative method can be applied to obtain Π which satisfies Eq. (13). Once Π is known, Q_i and C_i can be calculated from Eqs. (10) and (11)[9].

In this study, two different Freundlich-type isotherms were also applied to evaluate the adsorption equilibria and the results compared with those predicted by the IAS theory. One is an empirical multicomponent isotherm proposed by Fritz and Schlünder [3].

$$Q_i = A_i C_i^{(p_i + b_{ii})} / \{\sum_{j=1}^{N} a_{ij} C_j^{b_{ij}}\} \qquad (14)$$

where a_{ij} and b_{ij} are the inter-related parameters which must be determined from the multicomponent equilibrium data. The other isotherm was derived by Sheindorf et al.[4]. The form of this isotherm is:

$$Q_i = A_i C_i \{\sum_{j=1}^{N} \alpha_{ij} C_j\}^{(p_i - 1)} \qquad (15)$$

where α_{ij} is the competitive coefficient which may be calculated from the two-component adsorption data correlation.

EXPERIMENTAL

Materials

The adsorbates for study are phenol, p-chlorophenol (PCP) and p-nitrophenol (PNP). Stock solutions of each component were made up by dissolving reagent grade chemicals in distilled and activated carbon-filtered water. Multicomponent solutions were prepared by adding stock solutions that had been made up at varying concentrations.

The adsorbent used here was a commercial activated carbon supplied by Calgon Co. The physical properties are shown in Table 1. Prior to use, activated carbon particles were boiled and washed to remove impurities.

Equilibrium Experiments

Adsorption equilibrium data were obtained by in-

Table 1. Properties of activated carbon used.

Properties		Unit
Real density	2, 000	kg/m^3
Particle density	880	kg/m^3
Surface area (BET)	9.5×10^5	m^2/kg
Porosity	0. 56	
Mean pore radius	1. 34	nm
Particle diameter	0.9×10^{-3}	m

troducing known weight of activated carbon into $2x10^{-4}$ m^3 of mixed solution in Erlenmeyer flasks with stoppers and shaking in a constant temperature incubator at 20°C for 15 - 30 days to give sufficient contacting time for equilibrium. After equilibrium was obtained, a sample was taken from each flask. The concentrations of individual components were analyzed using an UV spectrophotometer in the range indicating a linear relationship between absorbance and concentration. For multicomponent systems, it was necessary to measure absorbances at different wavelengthes. 270, 280 and 314 nm were chosen in this study. The concentration of each component was then obtained by solving the corresponding Beer-Lambert equations with calibration constants.

RESULTS AND DISCUSSIONS

For single component systems, the adsorption equilibrium relations were represented by the Freundlich isotherm. The empirical parameters of single component isotherms are given in Table 2. The average percent deviations between measured and calculated values of amount adsorbed were less than 5% for single-range isotherms and less than 4% for two-range isotherms.

In the most of two-component systems, each component exhibits different adsorptivity because of affinity for activated carbon surfaces. Table 3 shows the parameters of two-component isotherms, Eqs. (14) and (15). Moon [10] reported that the affinity of a component increases as the value of exponent parameter of its single component Freundlich isotherm becomes small.
According to values shown in the first column of Table 2, the affinity of phenols for activated carbon used here increases in the order: phenol<PCP<PNP. The order of affinity is also confirmed by the value of the competitive coefficient of the Sheindorf's isotherm. Numerical value of α_{ij} is a measure of the competition effect between adsorbable components. The high value of α_{ij} means that the concentration of component j greatly affects the adsorption of component i but component i does not affect the adsorption of component j significantly. In this study, the key number of com-

Table 2. Single component Freundlich isotherm parameters.

	Single-range		Two-range			
	A_1	P_1	A_1	P_1	A_2	P_2
Phenol	1. 836	0. 206	–			
P C P	2. 496	0. 174	2. 379	0. 177	2. 387	0. 159
P N P	2. 374	0. 138	2. 438	0. 146	2. 353	0. 109

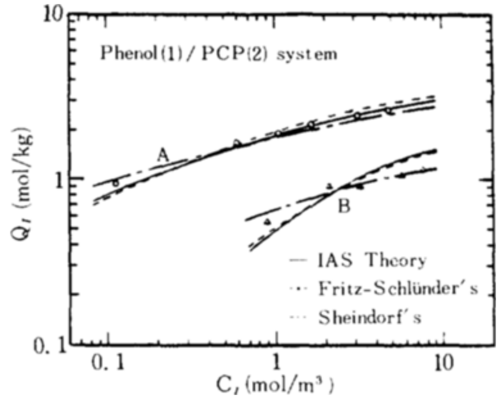

Fig. 1. Measured and predicted results for phenol(1)/PCP(2) system.

A : C_{PCP} with $C_{0,phenol} = 4.0 mol/m^3$
B : C_{phenol} with $C_{0,PCP} = 4.0 mol/m^3$

Table 3. Parameters of two-component isotherms.

Component (1)/(2)	Sheindorf's* α_{12}	Fritz-Schlünder's** a_{12}	a_{21}	b_{11}	b_{22}	b_{12}	b_{21}
Phenol/PCP	9. 27	3. 159	0. 700	0. 362	0. 222	0. 520	0. 408
Phenol/PNP	18. 03	7. 136	0. 802	0. 646	0. 051	0. 873	0. 714
PCP/PNP	1. 72	1. 308	0. 801	0. 630	0. 516	0. 884	0. 808

$^*\alpha_{ij} = \alpha_{ji}$ $\quad$ $^{**}a_{11} = a_{22} = 1$

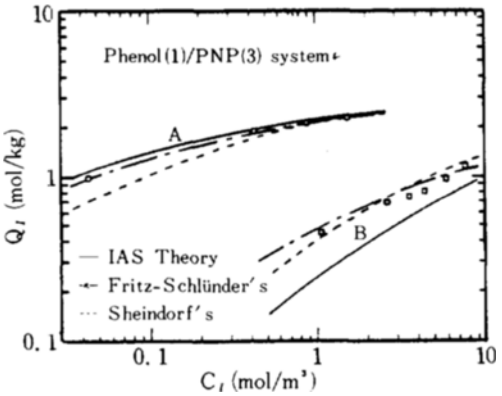

Fig. 2. Measured and predicted results for phenol(1)/PNP(3) system.

A : C_{PNP} with $C_{0,\,phenol}=4.0\,\mathrm{mol/m^3}$
B : C_{phenol} with $C_{0,\,PNP}=4.0\,\mathrm{mol/m^3}$

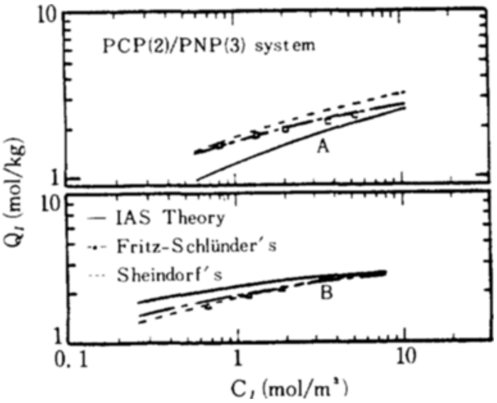

Fig. 3. Measured and predicted results for PCP(2)/PNP(3) system.

A : C_{PNP} with $C_{0,\,PCP}=2.0\,\mathrm{mol/m^3}$
B : C_{PCP} with $C_{0,\,PNP}=2.0\,\mathrm{mol/m^3}$

Table 4. Average percent deviations* of individual adsorptions.

Component (1)/(2)	Shenidorfs s_1	 s_2	Fritz-Schlünder's s_1	 s_2	IAS theory s_1	 s_2
Phenol/PCP	12.2	9.1	8.7	5.9	13.6	5.6
Phenol/PNP	9.6	3.3	5.3	3.7	21.6	4.5
PCP/PNP	17.5	4.3	7.1	2.2	17.5	4.3

* $s_i=\{\sum_{k=1}^{N}|Q_{i,\,pred}-Q_{i,\,meas}|\}/N$

ponents are ordered according to the affinity for activated carbon. Table 3 shows that α_{ij} of phenol/PCP and phenol/PNP systems are large values over 9 while that of PCP/PNP system becomes a low value near to unity. This fact shows that PCP and PNP have similar affinity for activated carbon. This difference could be interpreted by the interaction between the carbon surface and the functional groups of each component.

Fig. 1~3 show experimental and calculated equilibrium data of two-component systems. The broken lines represent values predicted by the Firtz-Schlünder's isotherm and the dotted lines do those predicted by the Sheindorf's isotherm. the solid lines stand for the IAS theory. The average percent deviations of two-component systems between measured and calculated results are shown in Table 4. In all cases, the Fritz-Schlünder's isotherm gives better predictions than the Sheindorf's isotherm and the IAS theory. The average percent deviation of the Fritz-Schlünder's isotherm is 2-10% while those of others are 5 - 24%. This is likely to be an inevitable result since the Fritz-Schlünder's isotherm contains many adjustable parameters to correlate two-component equilibrium data. For example, this isotherm for two-component systems has 6 independent inter-related parameters because a_{11} and a_{22} are unity. On the other hand, the Sheindorf's isotherm has only a parameter since $\alpha_{ij}=\alpha_{ji}$. When there are many adsorbable species in solution, it is nearly impossible to use the Fritz-Schlünder's isotherm because the determination of inter-related parameters gives rise to a serious difficulty. From this point, the Sheindorf's isotherm and the IAS theory have a good advantage of the use for multicomponent systems.

Fig. 1 ~ 3 show that the IAS theory and the Sheindorf's isotherm predict two-component equilibria with similar accuracy. The IAS theory has not an inter-related parameter besides single component equilibrium data. In this point, the use of the IAS theory is considered to be quite attractive for multicomponent adsorptions. Digiano et al. [7] presented a simple model for multicomponent equilibria which is based on the same concepts as in the IAS theory. This model allows direct computation of adsorbed amount from known concentrations in mixture, but it has a limitation that it is applicable only in a low concentration range less than 0.1 mol/m³. Such a limitation for the use of this simple model was also found in this study. In recent years, the species grouping has been studied to simplify the multicomponent adsorption calculation. It is, however, not easy to deduce some pseudo-species from a vast number of components because there are not appropriate grouping criteria. The adsorption and kinetic behaviors should be checked for the species grouping. [11]. On the other hand, the equilibrium relation must be easily incorporated with the model equations for the adsorption in batch or fixed bed adsorbers since the use of carbon adsorption requires information on the kinetic analysis of adsorption data. Thus, the adsorption isotherm should be examined, considering the incorporation with model equations as well as the accuracy in the prediction.

From discussions mentioned above, the IAS theory is the most convenient method at present for the prediction of multicomponent adsorption equilibria. The incorporation with mode equations has been examined by Merk et al.[12] and Wang and Tien [9]. They applied the IAS theory to two-component fixed bed adsorptions and obtained good results. In this study, one of the objectives is directed to the application of the IAS theory to three-component systems of phenols. Table 5 shows calculated and measured results of a three-component system using the Sheindorf's isotherm and the IAS theory. Φ_i in Table 5 represents the ratio of calculated to measured values of amount adsorbed. To show the applicability of IAS theory, the average percent deviations of two methods are also listed. For phenol/PCP/PNP system the deviations of the individual adsorption of each component are in the range of 6 -20% similar to those of two-component systems. Table 5 shows that two methods give quite similar accuracy in predicting three-component adsorption equilibria. It is very interesting that the IAS theory predicts equilibrium data with similar accuracy comparing with the Sheindorf's isotherm. This result proves that the IAS theory is quite

Table 5. Predictions of three-component adsorption equilibria.

Experimental						Sheindorf' s*			IAS Theory		
C_1	C_2	C_3	Q_1	Q_2	Q_3	Φ_1	Φ_2	Φ_3	Φ_1	Φ_2	Φ_3
3.090	2.430	1.260	0.276	1.270	1.516	0.945	1.279	0.801	0.878	0.828	1.038
5.271	5.523	3.895	0.327	1.283	1.722	0.633	1.309	0.956	0.697	0.890	1.077
5.181	4.709	2.285	0.327	1.471	1.406	0.816	1.278	0.915	0.864	0.879	1.118
5.179	3.729	3.311	0.329	1.029	1.774	0.749	1.353	0.978	0.770	0.876	1.096
5.033	3.033	1.826	0.365	1.232	1.499	0.908	1.275	0.901	0.887	0.832	1.103
5.315	3.189	1.327	0.324	1.491	1.215	1.185	1.208	0.886	1.174	0.821	1.160
5.250	3.143	2.444	0.381	1.068	1.713	0.792	1.331	0.915	0.783	0.855	1.064
5.221	2.844	1.721	0.376	1.163	1.512	0.954	1.323	0.882	0.922	0.860	1.085
4.796	1.932	0.833	0.464	1.276	1.165	1.062	1.233	0.853	0.970	0.813	1.170
5.151	2.062	1.522	0.395	0.997	1.546	1.043	1.316	0.905	0.955	0.823	1.103
4.930	1.671	0.879	0.468	1.106	1.305	1.117	1.276	0.835	0.993	0.817	1.115
4.446	5.176	3.615	0.226	1.332	1.708	0.820	1.257	0.954	0.889	0.849	1.085
4.328	4.269	2.065	0.247	1.534	1.489	0.980	1.211	0.915	1.016	0.826	1.133
4.408	5.168	2.141	0.301	1.656	1.387	0.749	1.232	0.857	0.805	0.864	1.072
4.550	3.749	3.471	0.212	1.152	1.879	1.002	1.193	0.949	1.031	0.770	1.057
4.313	2.983	1.872	0.268	1.312	1.553	1.064	1.184	0.896	1.033	0.768	1.092
4.324	3.126	1.682	0.307	1.459	1.447	0.956	1.142	0.885	0.935	0.753	1.107
4.410	3.154	1.420	0.301	1.639	1.269	1.052	1.083	0.902	1.034	0.728	1.168
4.207	2.326	1.690	0.273	1.169	1.646	1.153	1.182	0.876	1.071	0.743	1.062
4.065	2.097	1.182	0.367	1.242	1.438	0.993	1.202	0.849	0.905	0.768	1.093
3.984	1.980	0.887	0.422	1.362	1.239	0.958	1.171	0.842	0.871	0.765	1.146
4.391	2.048	1.930	0.275	0.988	1.779	1.163	1.205	0.905	1.064	0.736	1.055
4.010	1.654	1.151	0.409	1.054	1.523	0.960	1.230	0.864	0.840	0.758	1.089
3.901	1.390	0.725	0.456	1.169	1.304	1.059	1.179	0.815	0.908	0.744	1.113

Shenidorf's isotherm : $s_1=11.2$, $s_2=23.6$, $s_3=11.1$
IAS theory : $s_1=10.6$, $s_2=19.3$, $s_3=10.0$

$^*\Phi_i=Q_{i,pred}/Q_{i,meas}$

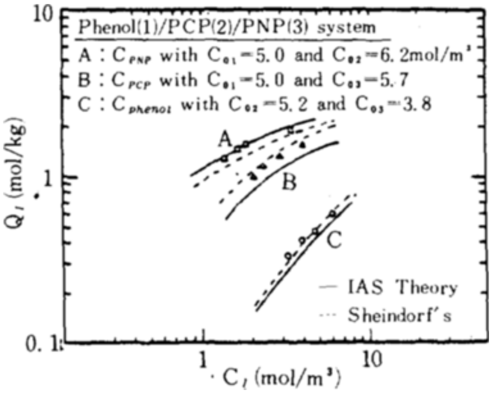

Fig. 4. Predictions of three-component equilibrium data.

suitable for phenols-activated carbon systems. At present, it is not clear if the IAS theory will give good predictions when the adsorbates have dissimilar equilibrium and kinetic behaviors. The extension of the IAS theory to such systems should be studied in the future. Fritz and Schlünder [8] reported that systematic deviations between measured and calculated results can be observed when there are ionic dissociation or molecular sieve effects. In the adsorption systems encountered here, these effects are negligible. Since pH of stock solutions is about 5~7 below the dissociation constant of phenols, the effect due to ionic dissociation is not significant during the adsorption.

In the application of the IAS theory, the most important thing is how to obtain accurate single component isotherms. The single component isotherm, sometimes, could not be represented by an equation. In this case, a piecewise isotherm or a combination from of some different isotherms may be used in representing single component equilibrium data over the concentration range. Here, the isotherms of PCP and PNP were divided into two regions which can be correlated by the Freundlich isotherm. Other isotherms can be also combined if an appropriate analytical relation between equations could be obtained. Fig. 4 shows a typical result of a three-component system in which some deviations between measured and calculated results are observed. However, such deviations may be insignificant for engineering-design applications considering experimental errors.

CONCLUSIONS

The IAS theory may be satisfactorily applied in predicting adsorption equilibria of phenols on activated carbon comparing with other Freundlich-type isotherms, the Fritz-Schlunder's isotherm and the Sheindorf's isotherm. Even for a three-component system, it gives good predictions. For phenols-activated carbon systems, ths IAS theory is likely to be quite suitable. According to the major advantage of the IAS theory which requires only single component equilibrium data, this theory will be the most effective method for the case that solution contains many adsorbable species.

NOMENCLATURE

A :surface area per unit mass of adsorbent (m^3/kg)
A_i :Freundlich isotherm parameter of component i
a_{ij} :parameters of Fritz-Schlünder's isotherm
b_{ij} :exponent parameter of Fritz-Schlünder's isotherm
C_i :equilibrium liquid phase concentration (mol/m^3)
$F(\pi)$:function defined in Eq. (13)
N :number of components
P_i :exponent parameter of Freundlich isotherm
Q_i :equilibrium solid phase concentration (mol/kg)
Q_t :total number of moles adsorbed (mol/kg)
R :universal gas constant
s_i :average percent deviation (%)
T :absolute temperature (K)
z_i :adsorbed phase mole fraction of component i

Greeks

α_{ij} :parameter of Sheindorf's isotherm
$\delta_{i,k}$:integration constant defined in Eq.(9)
Π :parameter defined in Eq.(8)
π_i :spreading pressure
Φ_i :ratio of calculated to measured values

Superscripts and Subscripts

o :single component state
i,j :components
k,m :concentration range
0 :initial concentration

Abbreviations

PCP :p-chlorophenol
PNP :p-nitrophenol

REFERENCES

1. Keith, L.H. and Telliard, W.: *Environ. Sci. Technol.*, **13,** 416 (1979).
2. Jain, J.S. and Snoeyink, V.L.: *J. WPCF*, **45,** 2463 (1973).
3. Fritz, W. and Schlünder, E.U.: *Chem. Engng Sci.*, **29,** 1279 (1974).
4. Sheindorf, C., Rebhun, M. and Sheintuch, M.: *J. Colloid Interface Sci.*, **79,** 136 (1981).
5. Myers, A.L. and Prausnitz, J.M.: *AIChE J.*, **11,** 121

(1965).

6. Radke, C.J. and Prausnitz, J.M: *AIChE J.*, **18,** 761 (1972).
7. Digiano, F.A., Baldauf, G., Frick, B. and Sontheimer, H.: *Chem. Engng. Sci.*, **33,** 1667 (1978).
8. Fritz, W. and Schlünder, E.U.: *Chem. Engng Sci.*, **36,** 721 (1981).
9. Wang, S.C. and Tien, C.: *AIChE J.*, **28,** 565 (1982).
10. Moon, H.: Ph. D. Thesis, KAIST, 1984.
11. Mehrotra, A.K. and Tien, C.: *Can. J. Chem. Engng*, **62,** 6321 (1984).
12. Merk, W., Fritz, W. and Schlünder, E. U.: *Chem, Engng Sci.*, **36,** 743 (1981).