This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Prediction of Multicomponent Adsorption Equilibria in Carboxylic Acid-Activated Carbon Systems

A. N. Goswami; A. Nanoti; S. K. Ganguly

To cite this Article Goswami, A. N. , Nanoti, A. and Ganguly, S. K.(1998) 'Prediction of Multicomponent Adsorption Equilibria in Carboxylic Acid-Activated Carbon Systems', Separation Science and Technology, 33: 11, 1617 — 1628

To link to this Article: DOI: 10.1080/01496399808545069

URL: http://dx.doi.org/10.1080/01496399808545069

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SEPARATION SCIENCE AND TECHNOLOGY, 33(11), pp. 1617–1628, 1998

Prediction of Multicomponent Adsorption Equilibria in Carboxylic Acid–Activated Carbon Systems

A. N. GOSWAMI,* A. NANOTI, and S. K. GANGULY
INDIAN INSTITUTE OF PETROLEUM
DEHRADUN-248005, INDIA

ABSTRACT

Binary adsorption equilibria of aqueous acetic and formic acid mixtures on activated carbon were measured. The multicomponent forms of the Langmuir, Langmuir–Freundlich isotherm, and the ideal adsorbed solution theory were used to predict the fluid phase and adsorbed phase concentration of components at equilibrium. Among the models tested, the ideal adsorbed solution theory gave uniformly satisfactory predictions both for liquid phase and for adsorbed phase compositions.

INTRODUCTION

Low molecular weight carboxylic acids like acetic and formic are present in wastewaters from several industries. Thus in the petrochemical industry, wastewater from a dimethyl terephthalate (DMT) plant contains up to 4 wt% acetic acid and around 5000 ppm formic acid. While these acids are not toxic, their removal is required before the wastewater can be discharged because of environmental limits (1). Moreover, these acids are important commodity chemicals and their recovery could be of economic importance.

Granular activated carbon has been used in industry for the removal of organics from wastewater. Toxic organics like phenols and chlorophenols have been successfully removed by this technique. A wastewater containing both phenol and acetic acid has been treated by carbon adsorption in a commercial plant of the Dow Chemical Company in the United States (2). Activated carbon adsorption is known to have a fair capacity for both acetic and formic acids, with acetic acid being the stronger adsorptive. There is scope

---

* To whom correspondence should be addressed.

www.dekker.com

for development of an adsorptive separation process based on activated carbon for removal of these acids from wastewaters.

For the design of a carbon adsorber for such an application, equilibrium isotherm data are required. Single component isotherms for both acetic and formic acids on carbon adsorbents have been reported (3, 4). However, to our knowledge the binary adsorption of mixtures of acetic and formic acid has not been studied.

In general, multicomponent adsorption studies have been rather limited partly because of difficulties associated with measurement of such data and also because of complexities involved in incorporating multicomponent equilibrium theories into adsorption calculations due to the implicit relationship between adsorbed and fluid phase composition in some of these theories.

Among multicomponent theories, the Langmuir (5), Langmuir–Freundlich, and the ideal adsorbed solution theory (IAST) (6) have the advantage of basing multicomponent predictions on single component isotherm parameters. In the present study the binary adsorption of acetic and formic acid mixtures has been measured on activated carbon, and the efficacy of the above theories in predicting these data has been investigated. The study forms part of our overall effort to develop a liquid-phase adsorption process to remove acetic and formic acids from petrochemical plant wastewaters.

As discussed by Tien (7), there are three types of adsorption calculations involving multicomponent theories:

1. Determination of the equilibrium adsorbed phase concentration of components given the equilibrium fluid phase composition.
2. Determination of the equilibrium fluid phase composition given the equilibrium adsorbed phase concentration.
3. Determination of both the fluid and adsorbed concentration of components at equilibrium given their initial concentrations in the feed mixture and the adsorbent dosage.

In the present study we have used the multicomponent adsorption theories to predict the adsorption equilibria under Condition 3 as given above. The basic material balance equation is

$$C_i + Wq_i = C_{i_0} \tag{1}$$

The multicomponent forms of the Langmuir and Langmuir–Freundlich isotherms are, respectively:

$$q_i = \frac{a_i C_i}{1 + \sum_{j=1}^{N} b_j C_j} \tag{2}$$

$$q_i = \frac{a_i C_i^{1/n_i}}{1 + \sum_{j=1}^{N} b_j C_j^{1/n_j}} \tag{3}$$

The ideal adsorbed solution theory is described by the following set of equations (7):

$$C_i = C_i^0(\Pi, T)x_i \tag{4}$$

$$\frac{\pi A}{RT} = \Pi = \int_0^{c_i^0} [q_i^0/C_i^0]dC_i^0 \tag{5}$$

$$q_T = \left[\sum_{i=1}^{N} x_i/q_i^0\right]^{-1} \tag{6}$$

$$\sum_{i=1}^{N} x_i = 1 \tag{7}$$

Adsorption calculations using these theories have been carried out by the methodology suggested by Tien (7).

EXPERIMENTAL

The acetic and formic acids used in this study were of 99.8% purity, supplied by M/s S.D. Chemicals Ltd. Bombay. Granular activated carbon (grade ICA) of surface area 999.6 m^2/g, supplied by M/s Industrial Carbons Pvt. Ltd. Baroda, was used as the adsorbent. The carbon was crushed prior to use, screened to 200–325 mesh, and washed with acid (0.05 N HCl) to leach out undesirable inorganics. This was followed by water washing with distilled water until the water extract was neutral to litmus. The carbon was then dried at 110°C for 4 hours and thereafter kept in a dessicator.

The equilibrium measurements were made using two different feed mixtures of acetic and formic acids: 0.5% acetic acid and 0.2% formic acid in one feed, and 1.0% acetic acid and 0.55 formic acid in the other. For each equilibrium adsorption measurement a binary mixture of acetic and formic acids of known composition was taken in a glass-jacketed stoppered vessel containing a known weight of crushed adsorbent sample. The experimental temperature was maintained at 30 ± 0.2°C by circulation of a thermostated liquid. The vessel was attached to a mechanical shaker and the contents were agitated for 4 hours. The solution was filtered, and the total acid content was determined by titration with standard alkali using phenolphthalein as indicator. The formic acid content in the filtrate was separately determined by ASTM D 3546-86 (8). The method involves determination of formic acid in aqueous acetic acid solutions by oxidation with lead tetraacetate. The accuracy of the analytical method has been checked and found to fall within ±3%.

RESULTS AND DISCUSSION

For the Langmuir isotherm, Tien (7) has defined the parameter D as

$$D = \sum_{j=1}^{N} b_jC_j \tag{8}$$

which, when used with the basic mass balance relationship, gives

$$C_i = \frac{C_{i_0}(1 + D)}{Wa_i + 1 + D} \tag{9}$$

Substituting for C_i in Eq. (8):

$$(1 + D)\left[\sum_{j=1}^{N} \frac{b_j C_{i_0}}{Wa_j + 1 + D}\right] - D = 0 \tag{10}$$

We used an iterative method scheme on the half-interval method (9) to derive D using this equation, from which value C_i and q_i could be calculated from Eqs. (9) and (2), respectively. For the Langmuir–Freundlich isotherm, a similar treatment gave the equilibrium fluid-phase composition as

$$C_i + Wa_i C_i^{1/n_i}/(1 + D) = C_{i_0} \tag{11}$$

where D is defined as

$$D = \sum_{j=1}^{N} b_j C_j^{1/n_j} \tag{12}$$

A double iteration scheme was used, first assuming a value for D and then using the half-interval method to estimate C_i. This was used in Eq. (12) to get a new estimate for D, and the process was continued until convergence was attained.

The pure component Langmuir and Langmuir–Freundlich parameters required in these calculations are summarized in Table 1. These parameters have been determined from adsorption isotherm measurements with pure components as reported earlier.

In implementing the IAST model the pure component isotherm data have been plotted on a sectional basis in Figs. 1A and 1B to conform to the Freundlich isotherm as suggested by Fritz and Schundler (10):

$$q_i^0 = A_{i_k}[C_{i_k}^0]^{1/n_{i_k}} \tag{13}$$

where A_i and n_i are the Freundlich parameters for the ith species over the

TABLE 1
Pure Component Adsorption Isotherm Parameters

	Langmuir		Langmuir–Freundlich		
Component	a_i	b_i	a_i	b_i	n_i
Formic acid	0.0309	0.0127	0.1785	0.0326	2.0455
Acetic acid	0.0487	0.0185	0.0893	0.0317	1.1913

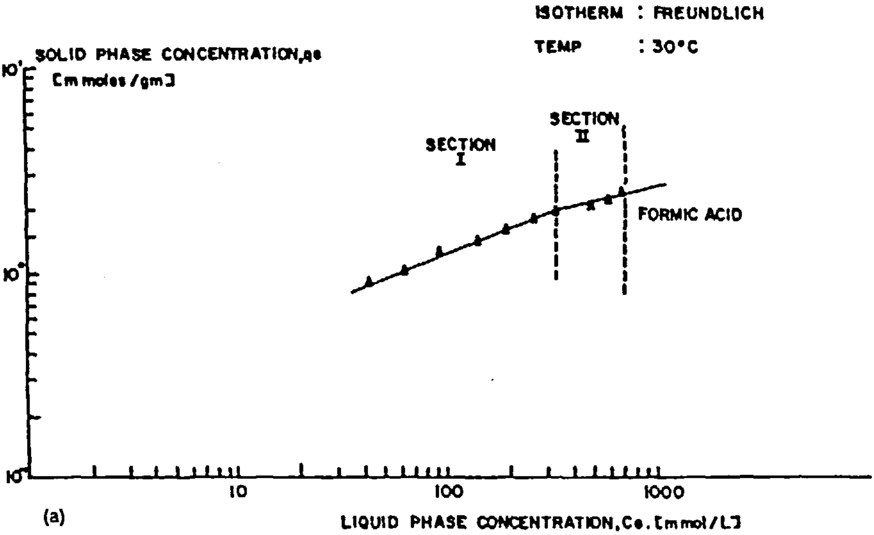

FIG. 1A Pure component Freundlich isotherm for formic acid–activated carbon system at 30°C.

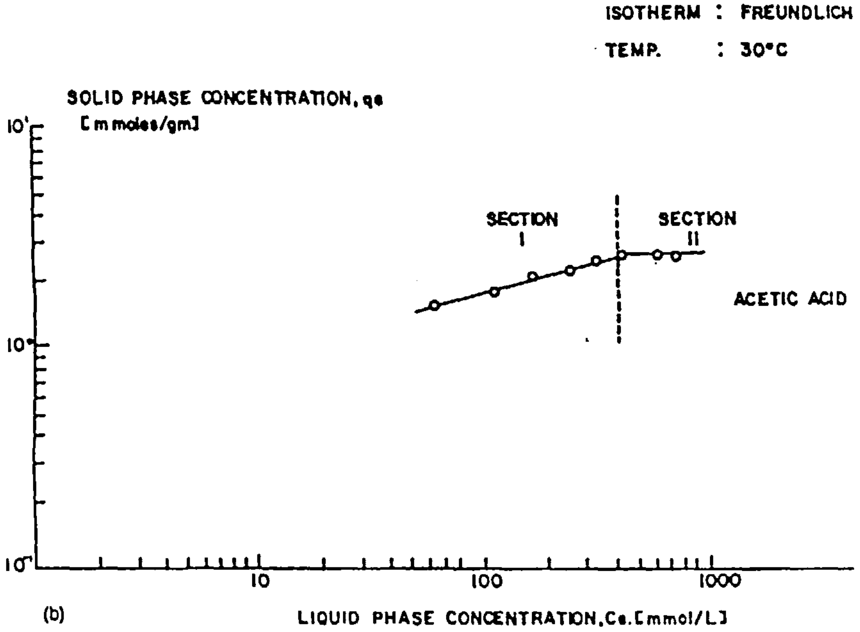

FIG. 1B Pure component Freundlich isotherm for acetic acid–activated carbon system at 30°C.

concentration range $C_{i_k} < C_i < C_{i_{k+1}}$. The IAST has the advantage that no restriction exists for the type of single component isotherm used in the multicomponent predictions. The isotherm that best fits the experimental data over the whole concentration range is the one to be used. When the Freundlich isotherm is taken on a sectional basis, extrapolation of the isotherm to regions of low surface coverage (where experimental data are generally not available) can be supported because the plot $d \ln c_i/d \ln q_i$ vs q_i extrapolates to unity. Two sections have been chosen for both formic acid and acetic acid. The Freundlich parameters for each section are given in Table 2. As has been worked out by Wang and Tien (11), the surface loading Π in the IAST model can be evaluated by solution of the following simultaneous equations:

$$1 - \sum_{i=1}^{N} \frac{C_{i_0}}{\left(\dfrac{\Pi + \delta_{i_k}}{A_{i_k} n_{i_k}} + \dfrac{W\Pi}{S}\right)} = 0 \tag{14}$$

$$\frac{\Pi}{S} - \sum_{j=1}^{N} \frac{n_{j_k}}{(\Pi + \delta_{j_k})} \frac{C_{i_0}}{\left(\dfrac{\Pi + \delta_{j_k}}{A_{j_k} n_{j_k}} + \dfrac{W\Pi}{S}\right)} = 0 \tag{15}$$

where

$$\delta_{i_k} = A_{i_k} n_{i_k} C_{i_k}^{0[1/n_{i_k}]} - \sum_{j=1}^{k-1} A_{i_j} n_{i_j} [C_{i_{j+1}}^{0[1/n_{i_j}]} - C_{i_j}^{0[1/n_{i_j}]}] - \left(\frac{1 + n_{i_1}}{2}\right) A_{i_1} C_{i_1}^{0[1/n_{i_1}]} \tag{16}$$

TABLE 2
Segment Maximum Concentration Limits and Freundlich Isotherm Parameters

Component: Formic Acid		
Segment, k	1	2
Maximum concentration C_i	336.9	697.8
Parameters:		
A_i	0.1753	0.4373
n_i	2.3151	3.8312

Component: Acetic Acid		
Segment, k	1	2
Maximum concentration C_i	426.3	712.4
Parameters:		
A_i	0.4697	0.5407
n_i	3.6271	4.0211

A Newton–Raphson iteration scheme was used to solve these equations. The equilibrium concentrations in the adsorbed and fluid phase were then calculated from the relationships

$$x_i = \frac{C_{i_0}}{\left[\dfrac{\Pi + \delta_{i_k}}{A_{i_k} n_{i_k}}\right]^{n_{i_k}} + \dfrac{W\Pi}{S}} \tag{17}$$

$$q_i = x_i \left[\sum_{j=1}^{N} \frac{x_j n_{j_k}}{\Pi + \delta_{j_k}}\right]^{-1} \tag{18}$$

$$C_i = x_i \left[\frac{\Pi + \delta_{i_k}}{A_{i_k} n_{i_k}}\right]^{n_{i_k}} \tag{19}$$

The relevant section k was chosen so that the calculated pure component concentration C_i^0 corresponding to surface loading fell within the limits of the segment.

In Figs. 2 to 4 we compare the experimental adsorbed and fluid-phase concentration for each component with the predicted values using the three models. The mean deviations reported in Table 3 have been calculated according to the formula

$$\sigma_i = \frac{1}{M} \sum_{K=1}^{N} \frac{|q_{i_{\mathrm{cal}}} - q_{i_{\mathrm{exp}}}|_K}{(q_{i_{\mathrm{exp}}})_K} \tag{20}$$

Among the three models, the IAST gives the most satisfactory predictions with mean deviations for the solid-phase composition falling around 0.09 for formic acid and 0.06 for acetic acid. Predictions for liquid-phase composition are much better, with mean deviations around 0.06 for both components. With multicomponent forms of the Langmuir and Langmuir-Freundlich isotherm models, deviations are much higher. For all three models, predictions of the concentration of a strong adsorptive (acetic acid) in the adsorbed phase are better than those of a weak adsorptive.

For multicomponent adsorption predictions the Langmuir isotherm is not always suitable because extension to the multicomponent form is based on the assumption of surface homogeneity with all sites likely to adsorb either solute. This may not be the case with adsorbents like activated carbons, as in the present case. The Freundlich isotherm is stated to be more suitable for pure component adsorption on heterogeneous adsorbents, but it is still an empirical expression and does not extrapolate to Henry's law at low concentration. The Langmuir–Freundlich isotherm provides greater flexibility, but its multicomponent equilibria predictions are seen to be worse when compared with the Langmuir isotherm.

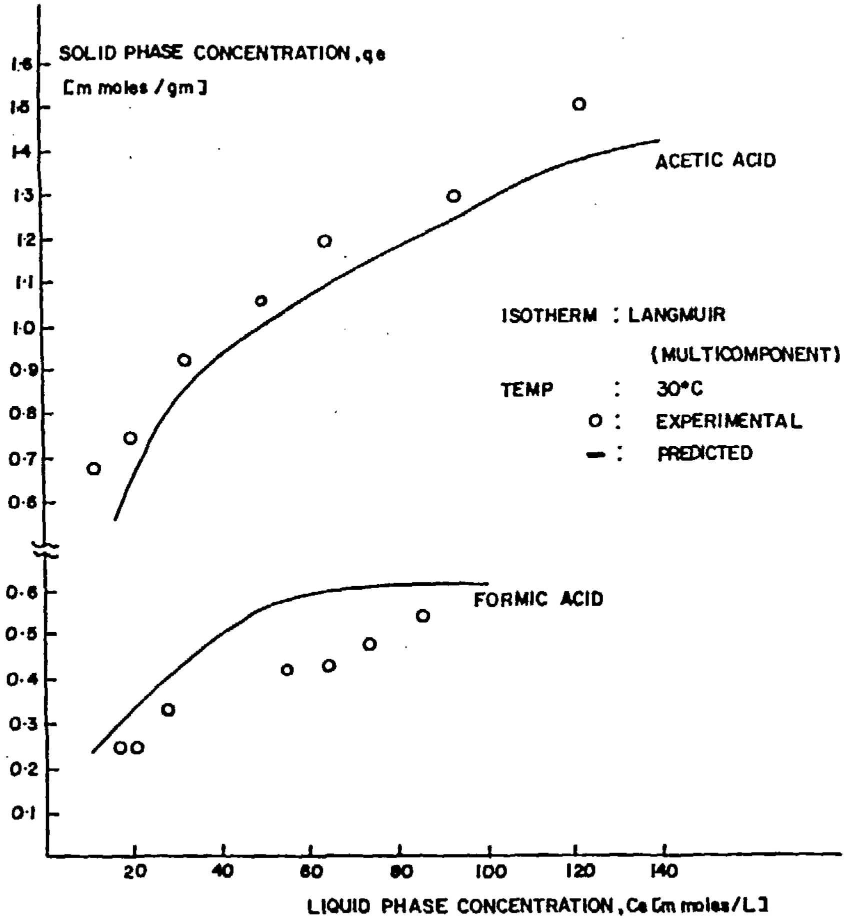

FIG. 2 Multicomponent Langmuir isotherm predictions for binary mixtures of formic and acetic acid-activated carbon system at 30°C.

The IAST has a sound theoretical basis. It is an application of solution thermodynamics to adsorption and as such it is independent of the actual model of physical adsorption. Moreover, it does not require any adsorption data for mixtures. As the results of this study show, it is the most suitable for multicomponent predictions of the three systems investigated.

CONCLUSION

Multicomponent adsorption equilibrium theories have been examined for prediction of binary adsorption equilibria of aqueous acetic and formic acid mixtures on activated carbon. Among the models tested the ideal adsorbed solution theory gave reasonably accurate predictions both for liquid and adsorbed phase compositions. A strong adsorptive concentration in the adsorbed phase is generally predicted with greater accuracy than a weak adsorptive.

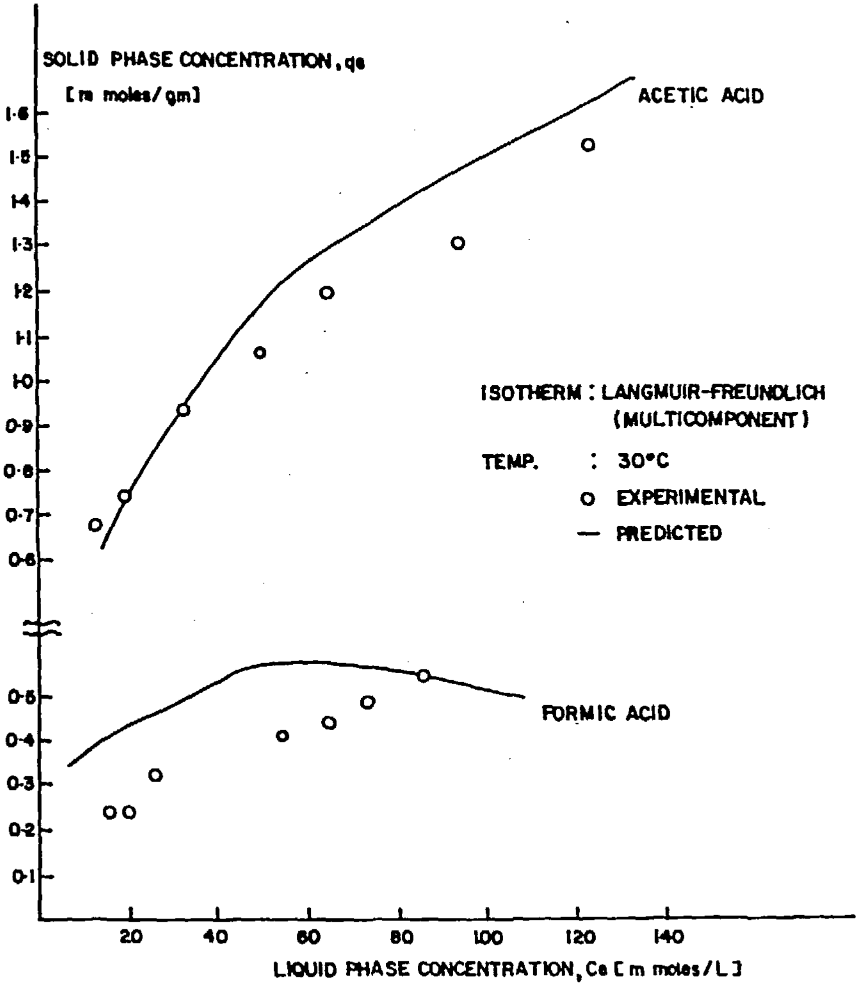

FIG. 3 Multicomponent Langmuir–Freundlich isotherm predictions for binary mixtures of formic and acetic acid–activated carbon system at 30°C.

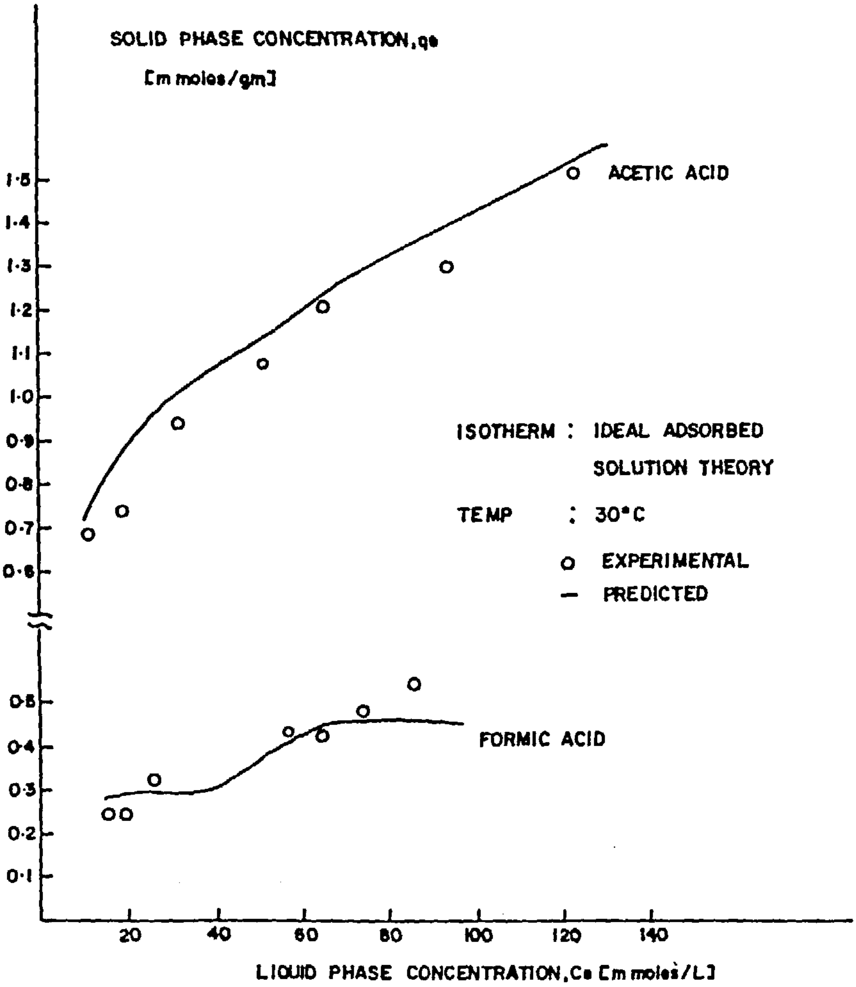

FIG. 4 Multicomponent isotherm using ideal adsorbed solution theory for predictions for binary mixtures of formic and acetic acid–activated carbon system at 30°C.

NOMENCLATURE

A	surface area per unit mass of adsorbent
A_i	Freundlich isotherm parameter of component i in segment
a_i	Langmuir isotherm parameter of component i

TABLE 3
Mean Deviations in Predicted Adsorbed and Liquid Phase Concentrations

	Mean deviation			
	Concentration of formic acid in		Concentration of acetic acid in	
Model	Adsorbed phase	Liquid phase	Adsorbed phase	Liquid phase
Langmuir	0.14	0.09	0.05	0.17
Langmuir–Freundlich	0.31	0.19	0.06	0.085
Ideal adsorbed solution theory	0.09	0.06	0.06	0.06

b_j	Langmuir isotherm parameter of component *j*
C_i	equilibrium liquid phase concentration of component *i*
C_{i_0}	initial concentration of *i* in feed mixture
C_i^0	concentration of *i* in liquid phase for pure component adsorption
D	parameter defined in Eq. (8)
N	number of components
n_i	Langmuir–Freundlich isotherm parameter
n_{i_k}	Freundlich isotherm parameter of component *i* in segment *k*
q_i	adsorbed phase concentration of component *i*
q_i^0	adsorbed phase composition of *i* for pure component adsorption
S	parameter defined in Eq. (15)
T	temperature
W	mass adsorbent used per unit volume of solution
x_i	mole fraction of component *i* in adsorbed phase

Greek Letters

δ	term defined in Eq. (16)
Π	surface loading
π	spreading pressure

REFERENCES

1. R. Cusack, *Chem. Eng. Prog.*, *92*, 56 (1996).
2. N. P. Cheremisinoff (Ed.), *Handbook of Heat and Mass Transfer, Vol. 2*, Gulf Publishing Co., Houston, TX, 1986, Chap. 3.
3. B. Baker and R. L. Pigford, *Ind. Eng. Chem. Fundam.*, *10*, 283 (1971).
4. F. E. Bartell and Y. Fu, *J. Phy. Chem.*, *33*, 676 (1929).
5. R. T. Yang, *Gas Separation* by *Adsorption*, Butterworths, Boston, MA, 1987, Chap. 3.

6. A. L. Myers and J. M. Prausnitz, *AIChE J.*, *11*, 121 (1965).
7. C. Tien, *Sep. Technol.*, *3*, 32 (1993).
8. *Annual Book of ASTM Standards*, Method D 3546–86.
9. B. Carnahen, H. A. Luther, and J. O. Wilkes; *Applied Numerical Methods*, Wiley, New York, NY, 1969, Chap. 3.
10. W. Fritz and E. U. Schlundler, *Chem. Eng. Sci.*, *36*, 721 (1981).
11. S. C. P. Wang and C. Tien, *AIChE J.*, *28*, 565 (1982).

Received by editor March 13, 1997
Revision received November 1997