Correction. Prediction of Multicomponent Adsorption Equilibria Using Ideal Adsorbed Solution Theory

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Prediction of Multicomponent Adsorption Equilibria Using Ideal Adsorbed Solution Theory

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■ The capability of ideal adsorbed solution theory (IAST) to predict multicomponent competitive interactions between the following volatile organic chemicals was tested: chloroform, bromoform, trichloroethene, tetrachloroethene, 1,2-dibromoethane, and chlorodibromomethane. A total of seven mixtures that contained various combinations of two, three, and six solutes were tested for three commercially available activated carbons. The predictions were satisfactory for the 256 isotherm data that were collected. An error analysis was performed for various isotherms that are used to represent single solute data in IAST calculations. This analysis demonstrated that the Freundlich equation was sufficiently accurate in representing the data under certain simplifying assumptions, and the use of the Freundlich equation in IAST calculations resulted in a relatively straightforward expression to describe the multicomponent data. The multicomponent data for the mixtures were plotted as total organic halogen (TOX) and total organic carbon (TOC), and, when the mixture data were plotted in this manner, appeared to behave as a pseudo single solute.

Introduction

A potentially useful technique for the removal of synthetic organic chemicals (SOCs) is adsorption onto granular activated carbon (GAC). The degree of removal of SOCs from drinking water or wastewater by GAC depends on the multicomponent competitive interactions of organic chemicals which are present in solution. In order to design a cost-effective system, the adsorption capacity of a solute in the presence of other solutes must be quantified. The design of GAC treatment systems using isotherm results such as those which are reported herein is discussed elsewhere (*1–11*).

Ideal adsorbed solution theory (IAST) has been used to predict the multicomponent equilibria of two components using their respective single-solute isotherm parameters (*10–17*). In this study, IAST was used to predict the multicomponent equilibria of up to six volatile organic compounds (VOCs) by using a simple algorithm. The identical algorithm has also been used to predict multicomponent equilibria of known adsorbates in unknown mixtures by using hypothetical components to represent

the adsorption strength of the background (*18–21*).

Materials and Experimental Methods

Chemicals. All chemicals were reagent grade or better. 1,2-Dibromoethane, bromoform, and chlorodibromomethane were obtained from Aldrich Chemical Co., Milwaukee, WI. Methanol, 2,2,4-trimethylpentane, chloroform, and trichloroethene were obtained from Burdick & Jackson Co., Muskegon, MI. Tetrachloroethane and 1,1,1-trichloroethane were obtained from J. T. Baker Chemical Co., Phillipsburg, NJ. Three activated carbons were used in these studies: Calgon's (Pittsburgh, PA) Filtrasorb-400 and Westvaco's (Covington, VA) WV-G and WV-W.

Chemical Analysis. The VOCs were analyzed by using gas chromatography with liquid–liquid extraction (LLE) and purge and trap methods (*22*). The samples for LLE method were extracted by using 5–30 mL of solution with 5–10 mL of 2,2,4-trimethylpentane following the procedure which was described by Mieure (*23*). 1,1,1-Trichloroethane was used as the internal standard for the LLE method. Hall, electron capture, and photoionization detectors were used for identification.

To determine the total organic halogen (TOX) of the isotherm mixtures, the gas chromatograph was used to quantify each halogenated species, and the total number of halogens in the various organic molecules was summed and expressed as chloride. This analytic procedure would give similar results to the actual procedure because Billet and Lichtenberg (*24*) have shown high TOX recovery for many of the solutes which were used in this study.

Isotherm Procedure. The equilibration time that was used satisfied the requirements which were discussed by Crittenden and Hand (*5*), Hand et al. (*6*), and Randtke and Snoeyink (*25*). A bottle point isotherm procedure was used to conduct all equilibrium studies. Carbon dosages, generally ranging from 6 to 3000 mg/L (1–500 mg in 160-mL bottles), were added to serum bottles that were then filled head space free with water containing the VOCs. The isotherm bottles were then rotated at 25 rpm and allowed to come to equilibrium.

Initial liquid-phase concentrations were determined by running blanks, with no carbon dosage, along with the samples. VOC loss, due to volatilization, was found to be negligible by comparing samples that were analyzed immediately to those that were equilibrated along with the samples.

Solutions were prepared with distilled, deionized Milli-Q water (Millipore Corp., Bedford, MA). The six-component

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isotherm experiment was conducted at 10–12 °C in a termperature-controlled room. The two- and three solute mixture isotherms were conducted at 20–22 °C. The solutions were buffered with a 0.001 M phosphate buffer at a pH of 6.0.

Once equilibrium was achieved, the PGAC was removed by centrifuging the isotherm bottles, and the liquid-phase concentrations were determined. The corresponding surface loadings were calculated from the following mass balance on an isotherm bottle:

$$q_i = (C_{i0} - C_i)V/M \qquad (1)$$

Carbon Preparation. Representative samples of the GAC were obtained by mixing and splitting the GAC. Powdered granular activated carbon (PGAC) which was within U.S. no. 200 and 400 sieves was used in the isotherm studies. PGAC was obtained by crushing representative samples of the U.S. no. 12 by 40-sieve carbon such that all of the crushed GAC passed the U.S. no. 200 sieve. The PGAC that was retained on a U.S. no. 400 sieve was then washed with Milli-Q water and dried overnight at 105 °C.

Approach

Ideal Adsorbed Solution Theory. In IAST, the following five basic equations are used to predict multicomponent behavior from single-solute isotherms (*12*):

$$q_T = \sum_{i=1}^{N} q_i \qquad (2)$$

$$z_i = q_i/q_T \qquad i = 1 \text{ to } N \qquad (3)$$

$$C_i = z_i C_i^0 \qquad i = 1 \text{ to } N \qquad (4)$$

$$1/q_T = \sum_{i=1}^{N} z_i/q_i^0 \qquad (5)$$

$$\frac{\pi_m A}{RT} = \int_0^{q_1^0} \frac{d \ln C_1^0}{d \ln q_1^0} dq_1^0 = \frac{\pi_1^0 A}{RT} =$$

$$\int_0^{q_j^0} \frac{d \ln C_j^0}{d \ln q_j^0} dq_j^0 = \frac{\pi_j^0 A}{RT} = \dots \text{ for } j = 2 \text{ to } N \quad (6)$$

Equation 2 defines q_T, the total surface loading. Equation 3 defines z_i, the mole fraction on the surface of the carbon for component i. Equation 4 is analogous to Raoult's law, where C_i^0 is the single-solute liquid-phase concentration in equilibrium with q_i^0. The single-solute surface loadings, q_i^0, are the loadings that cause the same spreading pressure, or reduction in surface tension, as the mixture. Equation 5 is the expression for no area change per mole upon mixing in the mixture from the single-solute isotherms at the spreading pressure of the mixture. Equation 6 equates the spreading pressures of the pure component systems to the spreading pressure of the mixture.

In this study, the single-solute isotherm representations which were proposed by Freundlich, Jossens et al. (*13*), and Singer and Yen (*14, 17*) were used in eq 6 to evaluate the spreading pressure.

Ideal Adsorbed Solution Theory Using the Freundlich Isotherm Equation. The Freundlich adsorption isotherm equation is given by the expression:

$$q_i = K_i C_i^{1/n_i} \qquad (7)$$

If the Freundlich isotherm equation is used to represent single-solute behavior in eq 6, then eq 6 will simplify to the expression:

$$n_1 q_1^0 = n_j q_j^0 \qquad j = 2 \text{ to } N \qquad (8)$$

After a great deal of algebraic manipulation, the following equation for each adsorbate was derived:

$$C_i = \frac{q_i}{\sum_{j=1}^{N} q_j} \left(\frac{\sum_{j=1}^{N} n_j q_j}{n_i K_i} \right)^{n_i} \qquad \text{for } i = 1 \text{ to } N \qquad (9)$$

Fritz et al. (*16*) reported an IAST algorithm that used a series of Freundlich parameters over various concentration ranges; accordingly, eq 9 may be considered a simplfication of their IAST equations. Equation 9 was combined with the mass balance, eq 1, to eliminate the liquid-phase concentration, C_i, in IAST predictions for bottle point isotherms as shown in the equation:

$$F_i(q_1, q_2, \dots, q_i, \dots q_N) = 0 =$$

$$C_{i0} - \frac{M}{V} q_i - \frac{q_i}{\sum_{j=1}^{N} q_j} \left(\frac{\sum_{j=1}^{N} n_j q_j}{n_i K_i} \right)^{n_i} \qquad \text{for } i = 1 \text{ to } N \quad (10)$$

According to eq 10, the equilibrium state in an isotherm bottle is determined by setting F_i equal to zero. Furthermore, all that is needed to define the equilibrium state are the Freundlich K and $1/n$, the initial concentration of each solute, and carbon dosage M/V. Since eq 10 is valid for all components, N nonlinear simultaneous equations with N unknown q_i values must be solved to estimate the final equilibrium state in the isotherm bottle.

This set of equations was solved by using a Newton–Raphson algorithm. If we let $\vec{q}_{new}$ equal the new guesses of $(q_1, q_2, q_i, q_N)^T$ (T is the mathematic operand known as transpose), $\vec{F}$ equal $(F_1, F_2, \dots, F_i, \dots F_N)^T$, and J^{-1} equal inverse of the Jacobian of eq 10, then the Newton–Raphson algorithm can be formulated by

$$\vec{q}_{new} = \vec{q}_{old} - J^{-1}_{old} \vec{F}_{old} \qquad (11)$$

in which, $\vec{q}_{new}$ and $\vec{q}_{old}$ are the new and old guesses to the roots of eq 10; $\vec{F}_{old}$ is the numerical value of eq 10 which is evaluated at $\vec{q}_{old}$. The off diagonal elements of the Jacobian are given by (eq 12 is valid for all i and k except when k equals i)

$$\frac{\partial \vec{F}_i(q)}{\partial q_k} = \frac{q_i}{(\sum_{j=1}^{N} q_j)^2} \left(\frac{\sum_{j=1}^{N} n_j q_j}{n_i K_i} \right)^{n_i} - \left(\frac{q_i n_i n_k}{\sum_{j=1}^{N} q_j} \right) \frac{(\sum_{j=1}^{N} n_j q_j)^{n_i - 1}}{(K_i n_i)^{n_i}}$$

$$(12)$$

The diagonal elements of the Jacobian are

$$\frac{\partial F_i(\vec{q})}{\partial q_i} = -\frac{M}{V} - \frac{1}{\sum_{j=1}^{N} q_j} \left(\frac{\sum_{j=1}^{N} n_j q_j}{n_i K_i} \right)^{n_i} +$$

$$\left[\frac{q_i}{(\sum_{j=1}^{N} q_j)^2} \right] \left(\frac{\sum_{j=1}^{N} n_j q_j}{n_i K_i} \right)^{n_i} - \left(\frac{q_i n_i^2}{\sum_{j=1}^{N} q_j} \right) \frac{(\sum_{j=1}^{N} n_j q_j)^{n_i - 1}}{(n_i K_i)^{n_i}} \quad (13)$$

To implement this algorithm, we start with an initial guess for $\vec{q}$ and improve our guess using eq 10–12 until eq 10 is satisfied. Usually four to six iterations are required to obtain greater than 0.01% precision in the roots to eq 10.

Table I. Summary of the Single-Component Isotherms, Experimental Conditions, and Freundlich Isotherm Parameters

carbon type, temp	compound	equilibration time, days, and pH	K, µg/g, $(L/µg)^{1/n}$ best fit	95% confidence interval K	K, µM/L, $(L/µM)^{1/n}$ best fit	95% confidence interval	$1/n$ best fit	95% confidence interval $1/n$	concn range, µg/L
F-400, 10-20 °C	cis-dichloroethene	7, 6.0	150.7	121.4-187.2	39.0	26.7-57.1	0.7045	0.6687-0.7402	120-1250
	trichloroethene	6.5, 6.0	3389.7	2795.6-4109.9	196.6	124.4-310.6	0.4163	0.3620-0.4706	5.6-360
	tetrachloroethene	6.0, 6.0	10388.8	9443.1-11429.2	650.6	530.1-798.9	0.4579	0.4365-0.4794	3.5-1170
	bromoform	10, 6.0	1802.0	1696.2-1914.4	160.5	142.9-180.3	0.5629	0.5528-0.5730	40.0-2000
	chloroform	7, 6.0	284.8	254.7-318.4	30.4	24.5-37.9	0.5325	0.5102-0.5549	8.0-1180
	1,2-dibromoethane	7, 6.0	1795.0	1632.6-1973.5	118.4	98.5-142.4	0.4808	0.4637-0.4979	32.0-1750
	chlorodibromomethane	7, 6.0	1265.7	981.7-1631.8	96.0	59.8-154.2	0.5170	0.4758-0.5581	92.0-1830
F-400, 20-22 °C	chloroform	2, 6.0	39.23	36.19-42.92	12.19	11.87-12.50	0.7556	0.7387-0.7725	34.5-1324
	trichloroethene	2, 6.0	1245	1012-1531	93.66	85.00-103.2	0.4696	0.4216-0.5177	3.2-528
	bromoform	2, 6.0	436.6	370.8-498.7	78.17	74.85-81.64	0.6889	0.6640-0.7139	11.8-3871
WV-G, 10-12 °C	cis-dichloroethene	7.0, 6.0	180.4	141.2-240.4	35.4	23.1-56.6	0.6441	0.6045-0.6383	143-1340
	trichloroethene	6.5, 6.0	3261.9	2986.9-3562.2	181.0	148.7-220.3	0.4073	0.3850-0.4295	5.3-120
	trichloroethene	3.0, 6.0	2847.0	2482.3-3265.3	148.4	107.3-205.1	0.3944	0.3561-0.4327	3.7-400
	tetrachloroethene	6.0, 6.0	7524.3	6700.6-8449.3	589.5	460.8-753.7	0.5017	0.4762-0.5271	7.0-910
WV-W, 20-22 °C	chloroform	2, 6.0	55.69	51.30-60.46	15.91	15.45-16.38	0.7380	0.7188-0.7571	4.2-947
	trichloroethene	2, 6.0	1062	816.7-1380.	92.84	82.12-105.0	0.5005	0.4399-0.5612	3-537
	bromoform	2, 6.0	474.6	401.8-560.6	64.82	64.60-67.28	0.6482	0.6236-0.6728	37-8092
HD 3000, 20-22 °C	chloroform	2, 6.0	92.48	88.63-96.52	19.12	18.90-19.34	0.6704	0.6612-0.6795	13.5-888
	trichloroethene	2, 6.0	712.8	479.2-1060	53.77	44.61-64.80	0.4702	0.3766-0.5637	4-585
	bromoform	2, 6.0	632.0	538.8-741.2	55.72	53.11-58.46	0.5608	0.5373-0.5843	46-8319
	chlorodibromomethane	2, 6.0	281.0	263.7-299.4	31.31	30.61-32.02	0.5890	0.5749-0.6031	14.5-510

Results and Discussion

Single-Solute Isotherms. The single-solute isotherm data were fit to the Freundlich adsorption isotherm equation. The data points were transformed by taking the logarithm of C_i and q_i, and the resulting values were fit by the least-squares method. Calculated values for K_i and $1/n_i$, along with upper and lower 95% confidence limits, are shown in Table I for the various GACs and adsorbates. Adsorption isotherms were conducted at two temperatures, 10-12 °C, which is a typical groundwater temperature in the Northern United States, and 20-22 °C. As shown in Table I, the adsorption capacities at 10-12 °C were approximately 2-4 times as high as those that were observed at 20-22 °C.

The time it takes for an isotherm to achieve equilibrium must be considered when conducting isotherms (5, 6, 25). Dobbs and Cohen (26) reported isotherm data that had been equilibrated for 2 h at 22 °C. This was not sufficient time to achieve equilibrium (5, 6, 25). For similar temperature, carbon, and adsorbates, capacities which were measured in this study was 2-3 times higher than were reported by Dobbs & Cohen (26) for all adsorbates except for bromoform. With a decrease in temperature to 10-12 °C, trichloroethane was still not at equilibrium until after 6 days. This was demonstrated by conducting long-term isotherms for 20 days. Consequently, 20-22 and 10-12 °C isotherm experiments were conducted for at least 2 and 6 days, respectively.

The agreement of the data to the Freundlich equation was expressed in terms of the average percent error (APE) in the fit:

$$APE = \frac{100}{N}\sum \frac{|X_{observed} - X_{predicted}|}{X_{observed}} \quad (14)$$

The isotherm data for 1,2-dibromoethane were described with excellent precision by the Freundlich isotherm with an APE of 3.9% in C and 1.1% in q. The isotherm data for trichloroethene had the most scatter of the single-solute isotherms with an APE of 14.9% in C and 1.5% in q. The single solute isotherm data for 1,2-dibromomethane and trichloroethene are shown in Figures 1 and 2, respectively.
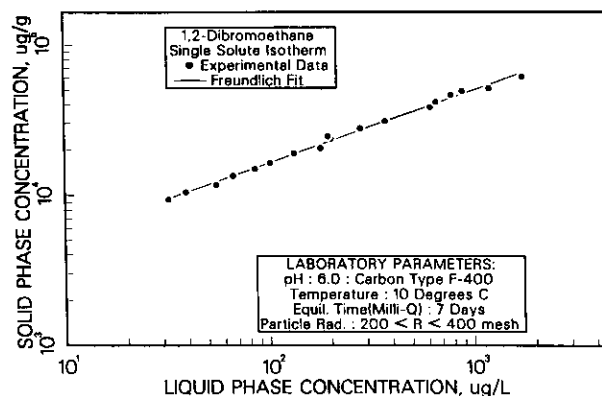

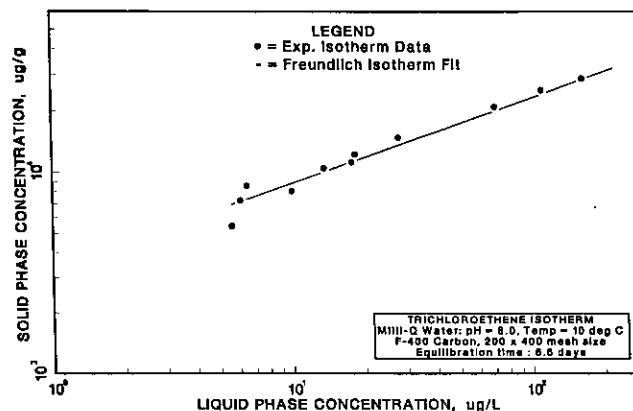**Figure 1.** 1,2-Dibromoethane isotherm data and the Freundlich isotherm fit for F-400 carbon.

Figure 2. Trichloroethene data and the Freundlich isotherm fit for F-400 carbon.

The dots are the experimental data and the solid lines are the Freundlich isotherm fits.

Analysis of Errors Associated with Using Ideal Adsorbed Solution Theory To Predict Multicomponent Equilibrium Using Various Single Solute Isotherms. Errors that arise from utilizing IAST are caused
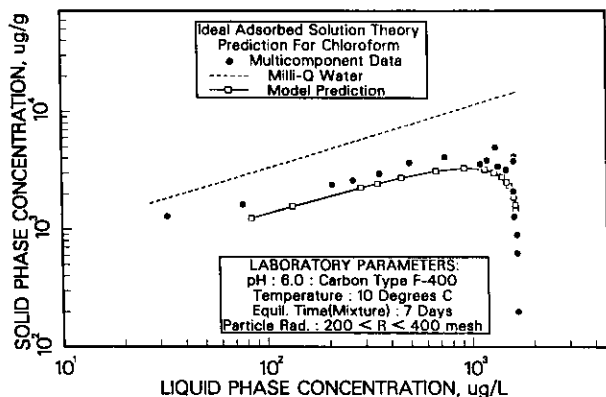
Figure 3. Chloroform isotherm data in the six-component mixture 7, IAST predictions using eq 10, and the single-solute isotherm.

Figure 4. 1,2-Dibromoethane isotherm data in the six-component mixture 7, IAST predictions using eq 10, and the single-solute isotherm.

Figure 5. Trichloroethene isotherm data in the six-component mixture 7, IAST predictions using eq 10, and the single-solute isotherm.

from extrapolating the single-solute isotherm data to zero and high concentrations. As shown in eq 6, a plot of d ln C_i^0/d ln q_i^0 vs. q_i^0 may be used to evaluate the importance of the single-solute isotherm on IAST predictions. Singer and Yen (14, 17) have proposed an isotherm that extrapolates the isotherm to low concentrations by assuming the isotherm is linear at a zero surface loading. However, IAST calculations that were made in this study using Singer and Yen's isotherm had a negligible effect on IAST calculations. Consequently, it was not used in IAST calculations because Freundlich IAST calculations which are given by eq 9 are much simpler to use.

With respect to extrapolation of single isotherms to high concentrations, IAST predictions often required single-solute surface loadings that were much higher than experienced in multisolute systems, particularly for the weakly adsorbed components. In spite of the fact that the single-solute isotherms were extrapolated, it is interesting to note that the IAST predictions for high surface concentrations were not any further off than the low concentration predictions.

Since no curvature was found in the single-solute isotherms when plotted on a log–log scale, the representations of the single-solute isotherms that account for curvature (10, 11, 13, 16) were not used to predict the VOC data.

Comparisons between Ideal Adsorbed Solution Theory Predictions and Multicomponent Volatile Organic Chemical Isotherm Data. As shown in Table II, isotherms were conducted for four bisolute mixtures, two ternary mixtures, and one six-component mixture to verify that IAST could predict multicomponent equilibria. All the raw isotherm data and IAST predictions for mixture 7 were presented by Luft (20). The information that is required for an IAST prediction using eq 9 is the Freundlich isotherm parameters, initial concentrations which are given in Table II, and the bottle volume and carbon dosages. For all the isotherm mixtures, the initial concentrations in the isotherm bottles were held constant, and the carbon dosages were varied to obtain the results. This procedure was used because this would be the situation that analysts would face in the field when they are estimating the capacity of GAC.

Table II also displays the APE in predicting C and q by using IAST. If all the 256 data are included, the APE which is defined by eq 14 was 29% and 16% for C and q, respectively. The greater precision in predicting q is expected because the isotherm slopes are close to 0.5 and errors in C would have less impact on q. Accordingly, multicomponent equilibria can be predicted satisfactorily by using eq 9.
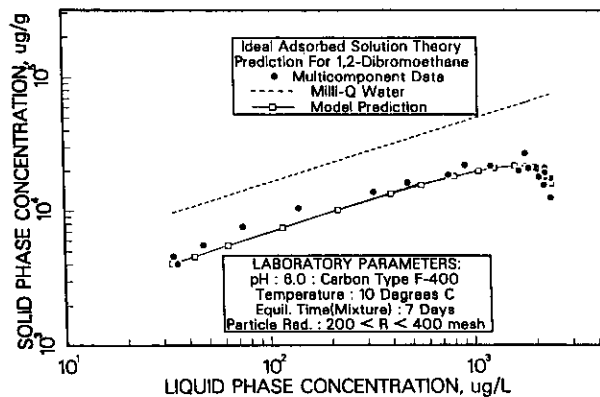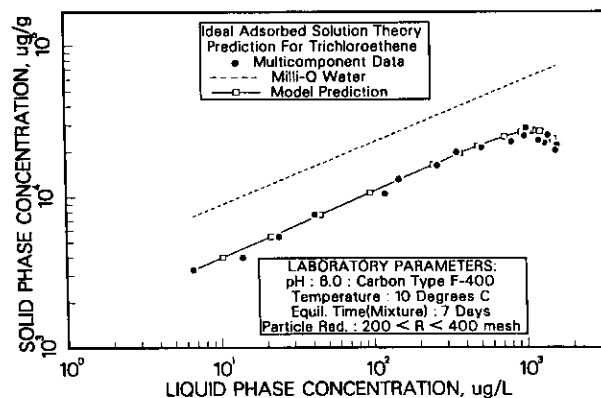
Figures 3–5 provide a visual representation of the pre-

cision of IAST predictions for three of the components in the six-component mixture (mixture 7 in Table II). The adsorbate chloroform, 1,2-dibromoethane, and trichloroethene, which are shown in Figures 3–5, are weakly, intermediately, and strongly adsorbing components in this mixture. The open boxes are the IAST predictions that correspond one to one with the data which are represented as solid dots. In cases where the prediction matches the data exactly, the dots hide the boxes. This displacement of the capacity which was observed in the mixture from the single-solute capacity can be seen by comparing the dashed lines which represent the single-solute isotherms to the data. This displacement is the greatest for higher liquid-phase concentrations or for small PGAC dosages because high surface concentrations of the strongly adsorbing components caused more competitive interactions.

On the basis of sensitivity analyses that were conducted by Luft (20) and the APEs that were observed in the single-solute isotherms, the IAST predictions were as precise as the experimental methods used to determine the single-solute isotherms. For example, the APE for TCE was 14% and 1.5% in C and q for the single-solute isotherms as contrasted to 22% and 4% in mixture 7. Therefore, no improvements in IAST predictions would be necessary until better methods could be obtained to measure single-component data.

Table III displays one set of the trisolute isotherm results and IAST predictions using the Freundlich isotherm equation. Also shown are the experimental relative adsorptivities which give the preference of component i as compared to component j by the adsorbent. The relative adsorptivity is defined by

$$\alpha_j^i = q_i C_j / (q_j C_i) \tag{15}$$

Table II. Average Percent Error between Experimental Multisolute Equilibrium Data and Ideal Adsorbed Solution Theory Predictions

mixture no.	carbon	temp, °C	components	initial concn in mixture, μM/L	relative % error using IAS — C	relative % error using IAS — q	no. of data	C range, μM/L	q range, μM/g
1	F-400	20–22	chloroform	11.8	12	11	22	1.46–10.2	12.8–29.5
			trichloroethene	12.4	44	4		0.019–3.33	15.4–182
2	F-400	20–22	chloroform	10.9	8	20	16	2.53–10.3	13.6–53.0
			trichloroethene	70.4	84	18		0.512–56.9	113–1151
3	WV-W	20–22	chloroform	9.76	21	21	22	0.276–9.03	4.39–19.7
			trichloroethene	45.2	12	2		0.0990–27.1	20.9–492
4	HD-3000	20–22	chloroform	8.46	57	67	24	2.07–7.25	7.61–27.3
			chlorodibromoethane	4.79	54	17		0.431–3.35	5.19–32.4
5	WV-W	20–22	chloroform	38.5	31	45	18	7.09–35.7	20.2–113
			trichloroethene	35.2	25	2		0.244–26.7	22.7–345
			bromoform	30.2	12	2		0.368–23.1	19.3–283
6	F-400	20–22	chloroform	38.5	22	30	23	4.16-37.4	15.7–82.1
			trichloroethene	35.4	24	2		0.102–30.6	16.2–389
			bromoform	30.2	27	15		0.198–27.0	13.8–256
7	F-400	10–12	chloroform	14.0	64	21	22	0.05–14	1.7–66
			trichloroethene	13.5	22	4	24	0.04–12.3	7.4–224
			chlorodibromoethane	12.4	24	13	24	0.13–11.9	6.7–128
			1,2-dibromoethane	13.4	22	8	24	0.13–12.7	7.3–146
			bromoform	11.4	19	12	23	0.07–10.9	6.5–195
			tetrachloroethene	12.3	45	4	14	0.04–5.4	95.7–915
			av % error for mixtures 1–7		29	16	256		
8[a]	B10-I		phenol		3	8	50		
			p-nitrophenol		47	1	50		
8[b]	B10-I		phenol		21	44	50		
			p-nitrophenol		1	28	50		

[a] Data of Fritz et al. (7), predicted by using the Jossens et al. (13) isotherm in IAST predictions. [b] Data of Fritz et al. (7), predicted by using eq 10.

According to Table III, the adsorbent prefers bromoform over chloroform by a factor of 4–18. It is interesting to note that the multicomponent Langmuir isotherm would predict a constant relative adsorptivity. Recently, Yen and Singer (17) demonstrated that the multicomponent Langmuir equation did not describe multicomponent equilibria for several phenols, whereas IAST was successful in describing the data.

Jossens et al. (13) presented IAST predictions for bisolute isotherm data that were collected by Fritz et al. (16). Since their data were collected at much higher concentrations, curvature was observed in their single-solute data, and the Jossens et al. isotherm equation was used to represent the single-solute isotherms in IAST calculations. The APE that was reported by Jossens et al. (13) was 2% in q; however, the APE in C was not reported. Bisolute data for phenol (initial concentrations 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, and 0.1 mM/L) and p-nitrophenol (initial concentrations of 0.02, 0.03, 0.04, 0.05, and 0.1 mM/L) were reanalyzed in this study by using the Jossens et al. isotherm in IAST calculations, and the APEs for q were 8% and 1% for phenol and p-nitrophenol, respectively. The APEs for C were 3% and 47% for phenol and p-nitrophenol, respectively. Jossens et al. (13) also reported 2–21% relative error for q in three other pairs of bisolute-substituted phenol data. Accordingly, the deviations from IAST which was found in this study were not significantly out of line with those reported by Jossens et al. (13) given the fact that this study was conducted at lower concentrations.

For the sake of mathematic expediency in fixed-bed model calculations, the curvature that is observed in the single-solute isotherm data may be ignored if less precision in the fixed-bed calculations can be tolerated. For example, the data which were predicted by Jossens et al. (13) isotherm were reanalyzed by fitting the Freundlich isotherm equation to the single-component data. Following this, eq 9 was used to predict their multicomponent isotherm data. As shown in Table II for mixture 8, the APE for C and q for phenol was 21% and 44% and for p-nitrophenol was 1% and 28% using the Freundlich isotherm as compared to 3% and 8% for phenol and 47% and 1% for p-nitrophenol, respectively, using the Jossens et al. isotherm. Consequently, one could use eq 9 to represent the data; however, the IAST predictions would not be as good.

TOC and TOX Isotherm Representations of Multicomponent Data. The multicomponent isotherm results for the various mixtures shown in Table II were expressed as single-component TOC and TOX isotherms, and their effective single-solute isotherms were evaluated. For example, according to these results, TOC or TOX isotherms of the various mixtures may appear to behave as pseudo single components. Figure 6 displays TOC and TOX isotherms for the trisolute mixture of chloroform, trichloroethene, and bromoform on F-400 carbon which was reported in Table II.

Conclusions

Ideal adsorbed solution theory (IAST) satisfactorily

Table III. Mixture 6 Equilibrium Data for Chloroform (Species 1), Bromoform (Species 2), and Trichloroethylene (Species 3), for F-400 Carbon and Initial Concentrations of 38.5 μM/L Chloroform, 30.2 μM/L Bromoform, and 35.4 μM/L TCE As Compared to IAS Predictions Using Equation 10

experimental surface concentration, μM/g			predicted surface concentration, μM/g			experimental solution concentration, μM/L			predicted solution concentration, μM/L			experimental relative adsorptivity	
q_1	q_2	q_3	q_1	q_2	q_3	C_1	C_2	C_3	C_1	C_2	C_3	α_1^2	α_1^3
82.1	256	389	80.8	491	353	37.4[a]	27.0[a]	30.6[a]	37.4	24.1	31.0	4.33	5.79
60.9	289	373	80.4	420	339	37.0[a]	23.2[a]	26.4[a]	36.5	20.0	27.1	7.58	8.58
57.7	281	323	80.0	365	322	36.4[a]	19.9[a]	23.7[a]	35.5	16.8	23.5	8.88	8.60
73.4	242	311	79.5	320	303	34.8[a]	18.2[a]	20.1[a]	34.5	14.2	20.2	6.32	7.33
99.8	205	287	79.0	288	286	32.4[a]	17.6	17.9[a]	33.6	12.4	17.7	3.78	5.21
81.0	213	272	78.4	258	268	32.5[a]	14.2	15.1[a]	32.5	10.8	15.2	6.02	7.20
55.7	193	238	77.5	227	296	33.3[a]	12.8	13.6[a]	31.2	9.09	12.5	8.98	10.5
47.2	161	206	75.8	188	212	32.7[a]	10.4	10.3[a]	29.1	7.02	9.16	10.7	13.9
39.5	140	176	73.6	157	182	32.5[a]	8.41	8.11[a]	26.9	5.49	6.67	13.7	17.8
38.1	120	156	71.4	137	161	31.4[a]	7.13	6.42[a]	25.0	4.52	5.14	13.9	20.0
40.0	113	141	69.1	121	143	29.8[a]	5.77	4.98[a]	23.3	3.80	4.06	14.6	21.1
40.9	93.1	115	64.4	97.5	116	27.1[a]	4.27	3.43[a]	20.3	2.80	2.65	14.5	22.3
43.8	86.8	106	62.3	89.4	107	25.0[a]	3.50	2.82[a]	19.1	2.47	2.22	14.2	21.5
39.5	64.3	78.9	53.9	65.8	76.7	21.5[a]	2.51	1.55	15.0	1.59	1.19	13.9	27.7
34.5	46.5	56.0	44.0	46.9	55.8	17.2[a]	1.48	0.890	11.0	0.977	0.589	15.6	31.2
32.1	36.6	43.7	37.1	36.6	43.4	12.9[a]	1.04	0.586	8.55	0.685	0.353	14.1	29.8
28.5	31.9	38.1	33.4	31.9	37.8	11.8[a]	0.779	0.388	7.37	0.561	0.264	17.0	40.6
26.3	27.4	32.6	29.6	27.3	32.3	10.1[a]	0.597	0.301	6.20	0.448	0.190	17.6	41.5
24.2	24.0	28.5	26.5	23.9	28.2	8.62[a]	0.494	0.213	5.33	0.370	0.144	17.3	47.7
22.0	21.6	24.9	24.2	21.5	25.3	7.42[a]	0.419	0.228	4.70	0.316	0.113	17.4	36.9
20.7	19.2	22.8	21.9	19.1	22.5	6.36	0.348	0.154	4.08	0.266	0.0880	17.0	45.2
17.8	16.1	18.9	18.7	16.0	18.8	5.47	0.285	0.263	3.28	0.204	0.0586	17.4	22.2
15.7	13.7	16.2	16.2	13.6	16.0	4.16	0.198	0.102	2.70	0.163	0.0425	18.4	42.0

[a] Extrapolated beyond existing single-solute isotherm data for evaluation of spreading pressure.
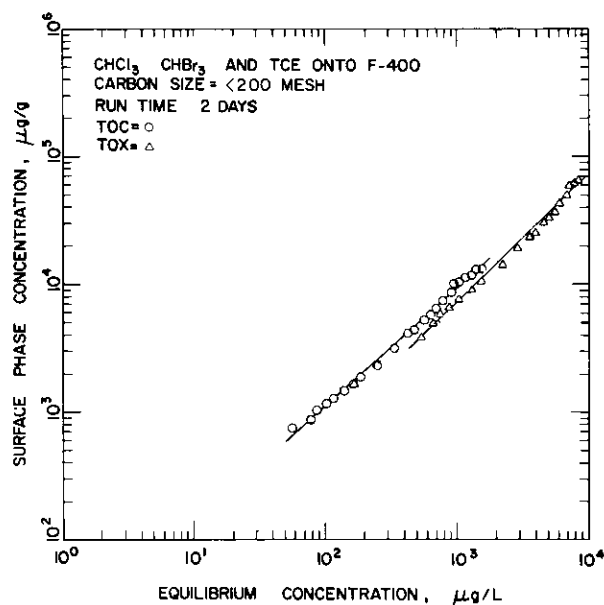
Figure 6. TOC and TOX (as Cl) isotherms for the trisolute mixture 6 which contains chloroform, bromoform, trichloroethene, and F-400 carbon.

predicted multicomponent competitive interactions between the following volatile organic chemicals: chloroform, bromoform, trichloroethene, tetrachloroethene, 1,2-dibromoethane, and chlorodibromomethane. A total of seven mixtures that contained various combinations of two, three, and six solutes were tested for three commercially available activated carbons. The average percent error was 29% and 16% for C and q, respectively, for the 256-multicomponent data that were collected. This amount of error is reasonable when compared to the precision of the single-solute data. However, these results are for relatively similar molecules, and more work is required to prove IAST can predict competitive interactions between

dissimilar adsorbates and adsorbates of different sizes.

An error analysis was performed for various isotherms that are used to represent single-solute data in IAST calculations. This analysis demonstrated that the Freundlich equation was sufficiently accurate to represent the data under certain simplifying assumptions, and the use of the Freundlich equations in IAST calculations resulted in a relatively simple expression to describe the multicomponent data. Accordingly, resulting IAST equilibrium expressions which are given by eq 9 can be sued if two conditions are met. First, the single-solute isotherm data cannot exhibit any curvature on a log–log scale. Second, extrapolation of the Freundlich isotherm equation to high and zero surface concentration must not result in significant errors in the calculation of the spreading pressure.

The multicomponent data for the mixtures were plotted as total organic halogen (TOX) and total organic carbon (TOC). When the mixture data were plotted in this manner, the mixture appeared to behave as a pseudo single solute.

Glossary

A	surface area of adsorbent per unit mass of adsorbent, L^2/M
C_i	liquid-phase concentration for component i, M/L^3
C_i^0	single-solute liquid-phase concentration for component i which is evaluated at the spreading pressure of the mixture, M/L^3
C_{0i}	initial liquid-phase concentration for component i, M/L^3
$\vec{F}_{old}$	vector of values of eq 10 which are evaluated at $\vec{q}_{old}$
$\vec{F}_{new}$	vector of values of eq 10 which are evaluated at $\vec{q}_{new}$
J	Jacobian of eq 10
J^{-1}	inverse of the Jacobian of eq 10
K_i	Freundlich capacity parameter for component i, $(M/M)(L^3/M)^{1/n}$
M	mass of carbon in isotherm bottle, M
N	number of components

$1/n_i$	Freundlich isotherm intensity parameter for component i, dimensionless
n_i	inverse of $1/n_i$
q_i	solid-phase concentration for component i, M/M
q_i^0	single-solute solid-phase concentration for component i which is evaluated at the spreading pressure of the mixture, M/M
$\vec{q}_{new}$	vector of the new guesses to the roots of eq 10, M/M
$\vec{q}_{old}$	vector of the old guesses to the roots of equation 10, M/M
q_T	total surface concentration, M/M
R	universal gas constant
T	absolute temperature
V	volume of isotherm bottle, L^3
z_i	mole fraction of component i adsorbed on surface, dimensionless

Greek

π_m	spreading pressure of the mixture
π_i^0	spreading pressure of the single solute i

Symbolic

$\rightarrow$	vector of values of a variable

Abbreviations

APE	relative percent error as defined in eq 14
DCE	*cis*-dichloroethene
EDB	1,2-dibromoethane
GAC	granular activated carbon
IAST	ideal adsorbed solution theory
LLE	liquid–liquid extraction
PGAC	powdered granular activated carbon
SOC	synthetic organic chemical
$\vec{F}^T$	transpose of vector $\vec{F}$
TCE	trichloroethene
TOC	total organic carbon
TOX	total organic halogen
VOC	volatile organic chemical

Registry No. C, 7440-44-0; chloroform, 67-66-3; bromoform, 75-25-2; trichloroethene, 79-01-6; tetrachloroethene, 127-18-4; 1,2-dibromoethane, 106-93-4; dibromochloromethane, 124-48-1.

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