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Adsorption of MTBE Vapors onto Activated Carbon[†]

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This work reports some experimental data on the adsorption of methyl *tert*-butyl ether (MTBE) and of 1-methylbutane vapors onto commercial activated carbon. 1-Methylbutane is assumed to simulate hydrocarbons present in vapor emissions from gasoline car tanks. Equilibrium adsorption data for MTBE + air and 1-methylbutane + air systems have been obtained from breakthrough curves and have been correlated by means of the Langmuir isotherm. Furthermore, the pseudoternary system MTBE + 1-methylbutane + air has been studied and the experimental competitive equilibrium data have been successfully compared with those obtained by ideal adsorbed solution theory. Experiments give information also on the kinetics of the adsorption operation. Modeling breakthrough curves allow the value of an overall mass transfer coefficient to be evaluated.

Introduction

Since 1970, methyl *tert*-butyl ether (MTBE) has been more and more widely used as a gasoline oxygenated additive as a substitute for tetraalkyllead as an octane number enhancer.

Further advantages deriving from the addition of MTBE into gasoline and highlighted in several recent studies are the possibility to decrease the percentage of aromatic compounds, like benzene, required to obtain an assigned octane number[1] and to improve combustion efficiency, which leads to lower CO and unburned hydrocarbon emissions at least at high engine loading.[2−4] Unfortunately, during engine cold-start, the presence of MTBE appears to produce higher emissions of HC, CO, and MTBE itself in exhaust gases.[4]

The present increasing attention toward environmental problems has highlighted the presence of increasing amounts of MTBE in the atmosphere and in aquatic environments, both in Europe and in America. MTBE is a toxic compound whose effects on human health are not yet well-known. Irritation symptoms on eyes or lungs have been observed and attributed to MTBE in countries where this compound is used as a gasoline additive.

Many studies have been devoted to identify the sources of this polluting compound in the environment, with special concern to shallow groundwater contamination. MTBE dispersion can result from point or diffused sources. Leaking underground storage tanks or wastes illegally discharged into the environment are some examples of liquid point sources. However, these sources do not account for the high MTBE concentration values observed in groundwater. Furthermore, if industrial or accidental liquid leakages were responsible of groundwater pollution, MTBE concentrations detected should be similar to those of other gasoline components whereas MTBE concentrations measured in aquatic environments are notably higher than those of the other components.

A possible mechanism able to account for these effects assumes atmospheric MTBE as responsible for the presence of this compound in shallow groundwater.[5,6] MTBE is a volatile compound released from gasoline in the vapor phase at a percentage higher than those for other volatile compounds. It can diffuse through ground in the vapor phase or can dissolve in rainwater and reach shallow groundwater by these two ways. This mechanism is supported by the widely observed contamination of water in urban areas with MTBE detected in the atmosphere near gasoline stations.[7] These observations indicate gas emissions released from motor vehicles and evaporation at gasoline stations during refueling as the main sources of MTBE in the environment.

Two main ways can be used to reduce pollution from volatile organic compounds (VOCs): the reduction of hydrocarbon concentration in exhaust gases and the lowering of vapor emissions at gasoline stations. The latter target could be achieved by adsorbing hydrocarbon and MTBE vapors onto activated carbon.

A device based on this unit operation could be easily designed and set up on cars where the carbon bed adsorbs MTBE and other VOC during refueling and is regenerated by air required for the normal working of the motor vehicle.

This work deals with the feasibility of this operation on the basis of the thermodynamic behavior of the system containing MTBE and hydrocarbon vapors in air. Unfortunately, scarce literature data[8−10] are available about adsorption, from mixtures with air, of MTBE vapors or, generally, of VOCs onto different adsorbent materials: in particular, poor information can be found about process kinetics. Therefore, experiments have been carried out with the 2-fold aim to obtain equilibrium adsorption data and to evaluate mass transfer properties in an adsorption column. The measurements of breakthrough curves for single solute and multisolute adsorption appear to be a suitable experimental procedure for obtaining both kinetic information and equilibrium isotherms. The accuracy of

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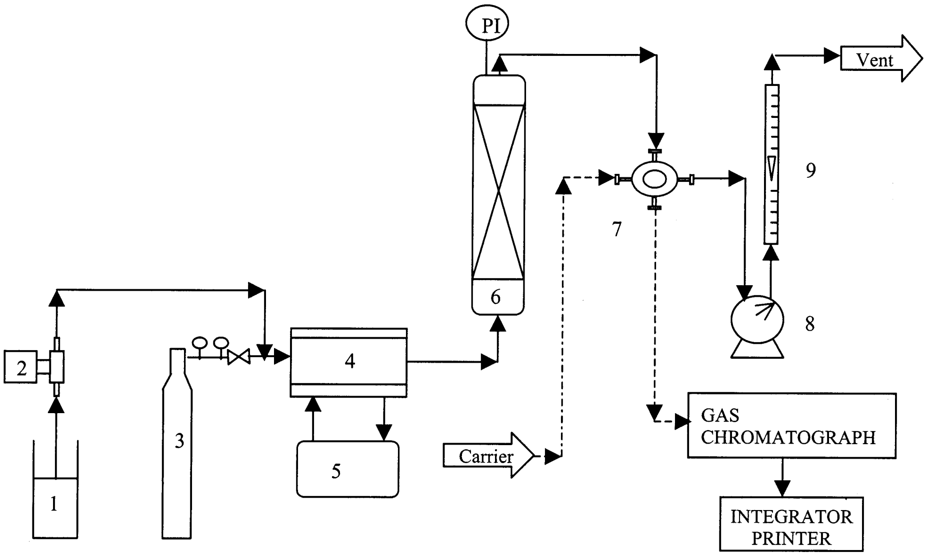

Figure 1. Experimental setup: (1) solute tank; (2) HP pump; (3) air cylinder; (4) evaporation chamber; (5) thermostatic bath; (6) adsorption column; (7) sampling and switching valve; (8) gas meter; (9) flow meter.

this method depends on the analytical precision in measuring the gaseous mixture composition as well as in more standard gravimetric methods when multisolute mixtures are adsorbed.

Experimental Section

Materials and Analytical Procedure. Granular commercial activated carbon with mean particle diameters equal to 1.5 mm was used as adsorbent material. The activated carbon was supplied from Merck and showed a specific surface area of 1600 m^2/g, a porosity of 1.5 cm^3/g, and an apparent density of 0.4 g/cm^3. MTBE and 1-methylbutane were supplied from Aldrich and showed a purity equal to 99.8% and 99.5% by mass, respectively.

Analytical Procedure. In all experiments, gas composition was measured by means of gas-chromatographic analysis using an HP 5860 gas-chromatograph equipped with a flame ionization detector (FID). Solute peaks were resolved very well by means of a POROPAK Q 80/100 mesh (length 2 m) capillary column with the following operative conditions: injection temperature, 523 K; oven temperature, 473 K; detector temperature, 523 K; carrier gas, He at 30 cm^3/min. The calibration of the instrument was carried out by injecting solutions with different known solute concentrations and by recording the peak area. The experiments were carried out in the linear response range of the detector.

The analysis of each sample of unknown concentration was repeated five times, and the readings were averaged. Mean values of uncertainty in solute concentrations equal to ±4.3% and to ±7.5% were estimated for MTBE and 1-methylbutane, respectively.

Apparatus. A continuous laboratory apparatus was used to obtain breakthrough curves: a schematic diagram of the experimental setup is presented in Figure 1. It consists essentially of a glass column, an evaporation chamber, a manual sampling and switching valve, an HPLC pump, a flow meter, and a volumetric gas meter.

All experimental runs were performed with dry air taken from a gas cylinder at a constant flow rate whereas solute flow rates were changed in order to prepare solutions at different solute concentrations. For two-solute adsorption tests, liquid binary solutions were utilized. Unfortunately, our equipment did not allow an air−VOC mixture at low solute concentration to be prepared with satisfactory accuracy.

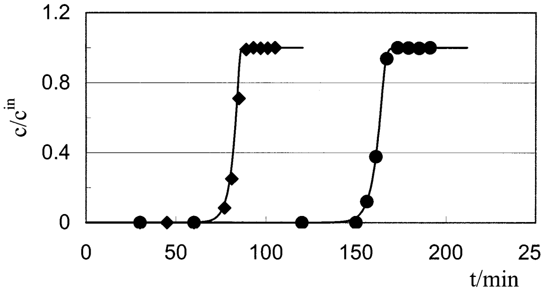

Figure 2. Breakthrough curves of binary mixtures: ●, exp MTBE, $c^{in} = 56\ mg \cdot L^{-1}$; ◆, exp 1-methylbutane, $c^{in} = 94\ mg \cdot L^{-1}$).

Solute and air were fed to the evaporation chamber, kept at (323 ± 0.1 K) in order to obtain the complete vaporization of the solute, and then sent onto the adsorption column (25 mm i.d., 100 mm height), filled with about 12 g of activated carbon. The column was equipped with a Teflon septum, which supports the adsorption bed and distributes the gas over the whole section of the column, and with a 10 mm layer of glass wool at the top in order to prevent the entrainment of solid particles. Pressures in the range 1.2−1.3 atm were detected at the top of the column.

The air−solute stream from the column was fed to a manual sampling and switching valve equipped with a stainless steel sample loop volume (250 μL). The stream was sent to the flow meter and to the volumetric gas meter to register the gas flow rate and the total amount of air used in the experimental run (gas volume was measured with a precision of ±10 cm^3). At fixed times, the stream was diverted to the gas-chromatograph in order to determine its composition.

Results

Figure 2 shows the typical trend of a breakthrough curve for MTBE + air and 1-methylbutane + air mixtures. Figure 3 is a plot of a breakthrough curve measured for the ternary mixture containing both MTBE (1) and 1-methylbutane (2) in air. The MTBE concentration in the outlet stream increases uniformly up to the inlet value, when bed saturation conditions are reached. The behavior of 1-methylbutane is more complex. Its concentration in the outlet

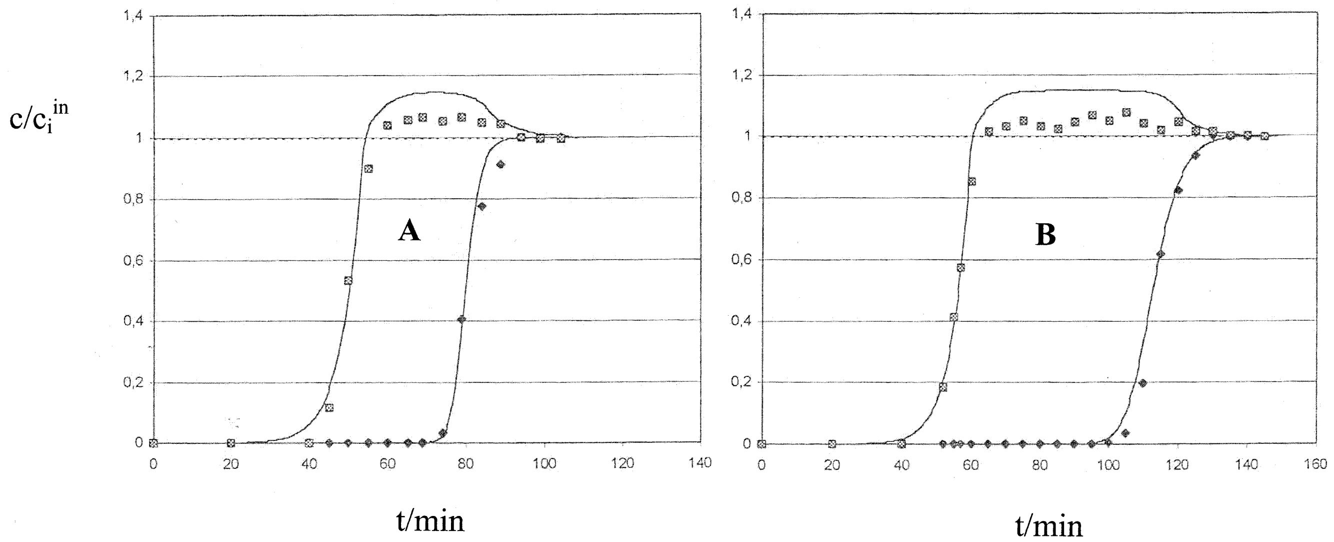

Figure 3. Breakthrough curves of ternary mixtures. A: ■, $c_1^{\text{in}} = 84$ mg·L^{-1}; ◆, $c_2^{\text{in}} = 71$ mg·L^{-1}. B: ■, $c_1^{\text{in}} = 37$ mg·L^{-1}; ◆, $c_2^{\text{in}} = 71$ mg·L^{-1}. Solid line: IAS model.

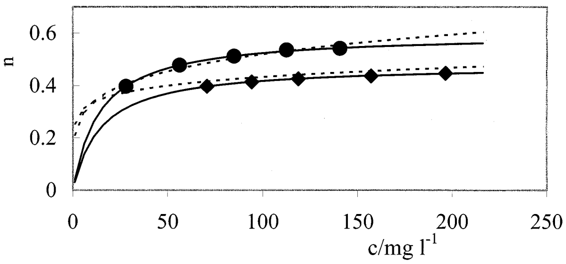

Figure 4. Adsorption equilibrium data: dotted lines, Freundlich isotherm; solid lines, Langmuir isotherm; ●, exp MTBE; ◆, exp 1-methylbutane.

stream increases more quickly than that of MTBE, overcoming its inlet value for some time. Then it comes back to the inlet value. This behavior, which is more apparent the greater the 1-methylbutane inlet flow rate is, can be explained by preferential adsorption of MTBE in the first zone of the column, whereas 1-methylbutane is retained in the upper layers of the adsorbent. The progressive saturation of the solid bed by MTBE causes the displacement of the previously adsorbed 1-methylbutane.

Binary breakthrough curves can be used to calculate the amount M of adsorbed solute:

$$M = Wc^{\text{in}}t_{\text{r}} - \int_0^{t_{\text{r}}} Wcdt \qquad (1)$$

where c^{in} is the inlet flow concentration, c is the effluent concentration, W is the volumetric flow rate, and t_{r} is the time when the adsorption breakthrough is reached. In eq 1 the amount of solute entrapped in the bed porosity was considered negligible, as the solute concentration in vapor phase was quite low. Division of M by the mass of activated carbon in the column (determined gravimetrically) results in the adsorbed values as gram of contaminant per gram of activated carbon. Analysis of the experiments at different inlet concentrations by the above procedure enables the construction of the adsorption isotherm (see Figure 4).

An evaluation of the error propagation in the adsorbed amounts yields an average error of ±5.3% for MTBE and of ±8.5% for 1-methylbutane, slightly higher than the uncertainties in solute concentration measurements.

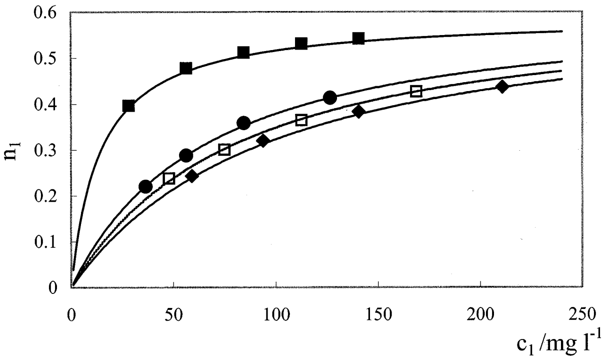

Figure 5. Ternary system MTBE (1) + 1-methylbutane (2) + air: specific adsorbed amount of MTBE vs MTBE equilibrium concentration at different inlet concentrations of 1-methylbutane (■, $c_2^{\text{in}} = 0$ mg·L^{-1}; ●, $c_2^{\text{in}} = 71$ mg·L^{-1}; □, $c_2^{\text{in}} = 94$ mg·L^{-1}; ◆, $c_2^{\text{in}} = 118$ mg·L^{-1}).

Table 1. Mixtures Air + MTBE and Air + 1-Methylbutane: Adsorption Capacity of Activated Carbon (*n*, Mass of Solute per Unit Mass of Activated Carbon) at Different Solute Concentrations (*c*, mg·L^{-1})

MTBE + air mixtures		1-methylbutane + air mixtures	
c	*n*	*c*	*n*
28	0.40	70	0.39
56	0.48	94	0.41
84	0.51	118	0.43
112	0.53	157	0.44
141	0.54	196	0.45

Table 1 reports specific adsorbed amounts (i.e. mass of solute per unit mass of activated carbon), for MTBE + air and 1-methylbutane + air mixtures, at several solute concentrations. These results show that MTBE is adsorbed 15−20% more than 1-methylbutane.

Figure 5 is a plot of adsorption isotherms for the ternary mixtures MTBE (1) + 1-methylbutane (2) + air at different inlet concentrations of 1-methylbutane (Table 2). An average error of ±5.3% is estimated in adsorbed amount of MTBE. We can observe that the carbon capacity to adsorb MTBE decreases with increasing 1-methylbutane concentration in the vapor mixture.

Discussion

Correlation of Equilibrium Data.

(1) Single Solute Mixtures. Single solute equilibrium data were correlated by means of Freundlich and Langmuir

Table 2. Mixtures MTBE (1) + 1-Methylbutane (2) + Air: Multicomponent Adsorption Equilibrium Data (*n*, Mass of Solute per Unit Mass of Activated Carbon at Different Solute Concentrations (*c*, mg·L^{-1})

$c_2 = 71$		$c_2 = 94$		$c_2 = 118$	
c_1	n_1	c_1	n_1	c_1	n_1
37	0.42	48	0.48	59	0.48
56	0.46	75	0.49	94	0.54
84	0.54	112	0.53	141	0.55
126	0.55	169	0.56	211	0.57

Table 3. Values of Freundlich and Langmuir Parameters and Root Mean Square Deviations for the Systems MTBE + Air and 1-Methylbutane + Air

parameter	air + MTBE	air + 1-methylbutane	isotherm
k_F, mg^{-1}·L	3.47×10^{-4}	6.91×10^{-2}	Freundlich
p	0.1949	0.1152	
rmsd	1.02×10^{-2}	1.76×10^{-2}	
$n_{\max}$	0.5983	0.4797	Langmuir
k, mg·L^{-1}	14.2226	14.8663	
rmsd	5.77×10^{-4}	8.02×10^{-4}	

isotherms:

$$n = (k_F c)^p \tag{2}$$

$$n = n_M \frac{c}{k + c} \tag{3}$$

where n is the specific adsorbed amount, c is the concentration in the gaseous phase, k_F and p are parameters in the Freudlich equation, and n_M and k are parameters in the Langmuir equation.

Isotherm parameters were evaluated from fitting of experimental data, using the least-squares method. The values obtained are reported in Table 3 together with root mean square deviations (rmsd's) whereas fitted curves and experimental data are compared in Figure 4. For the reason mentioned in the Apparatus section, experiments refer to quite high solute concentrations. Lower values could be more useful for discriminating between the two models. However, on the basis of our results, the Langmuir isotherm appears to give a better correlation of the experimental data for both components.

(2) MTBE (1) + 1-Methylbutane (2) + Air Mixtures. Experimental results of multisolute adsorption isotherms were correlated by the thermodynamic model of Radke and Prausnitz.[11] This method, which is based on the hypothesis of ideality of the adsorbed phase (IAS), is completely predictive because it allows the specific adsorbed amount of different compounds to be evaluated once the adsorption isotherm of each component is known. According to this approach, the following relationship holds between the mole fraction (on a solvent-free basis) of solute i in the adsorbed phase, z_i, and the concentration of the same solute in the gaseous phase, c_i:

$$c_i = z_i c_i^\circ \tag{4}$$

where c_i° is the concentration of i in a gaseous phase containing only the i solute at the same temperature and dimensionless spreading pressure (π) as those for the mixture. Details of the procedure to derive the relationship between c_i° and π are reported elsewhere.[12] For the Langmuir isotherm, we get

$$c_i^\circ = k_i(e^{\pi/k_i} - 1) \tag{5}$$

$$z_i = \frac{c_i}{k_i(e^{\pi/k_i} - 1)} \tag{6}$$

The value of π can be calculated by imposing the constraint that the sum of the mole fractions of all the solutes in the adsorbed phase must be 1:

$$\sum_{i=1}^{nc} \frac{c_i}{c_i^\circ} = 1 \tag{7}$$

Once the spreading pressure of the mixture has been obtained, c_i° and n_i°, that is, the concentration of i in the gaseous phase and the specific adsorbed amount of i in a system containing only the i solute at the same temperature and spreading pressure as those for the mixture, can be determined straightforwardly.

In particular, in the case of the Langmuir equation, n_i° is given by

$$n_i^\circ = n_{Mi} \frac{c_i^\circ}{c_i^\circ + k_i} \tag{8}$$

Finally, by means of the IAS model, the total adsorbed amount, n_T, is given by

$$\frac{1}{n_T} = \sum_{i=1}^{nc} \frac{z_i}{n_i^\circ} \tag{9}$$

and the specific adsorbed amount of i from the multisolute solution, n_i, is obtained:

$$n_i = z_i n_T \tag{10}$$

Figure 5 reports a comparison between theoretical and experimental values of the adsorbed amounts of MTBE (n_1) at different equilibrium concentrations of MTBE (c_1): the agreement is good for each value of the inlet concentration of 1-methylbutane.

Correlation of Kinetic Data. By means of differential mass balances for vapor and solid phases, and the mass transfer condition from the vapor to the solid phase, it is possible to model the dynamic behavior of an adsorbing bed.[13]

In the hypothesis of an isothermal plug flow, the following differential equation is obtained:

$$v\left(\frac{\partial c}{\partial z}\right)_t + \epsilon\left(\frac{\partial c}{\partial t}\right)_z + (1 - \epsilon)\frac{3}{R}K(c - c_s) = 0 \tag{11}$$

where c is the concentration, in the fluid phase, of solute i at time t and at distance z from the bed inlet, c_s is the equilibrium concentration of i at the adsorption temperature, ϵ is the bed porosity, R is the radius of the particles of activated carbon, and v is the fluid velocity in the bed. The last term in eq 11 refers to the solute transfer from the vapor to the adsorbed phase. The parameter K is an overall mass transfer coefficient that accounts for vapor-phase and solid-phase resistances.

A differential mass balance in the solid phase gets to the following equation:

$$\rho\left(\frac{\partial n}{\partial t}\right)_z = \frac{3}{R}K(c_s - c) \tag{12}$$

where n is the specific adsorbed amount at z and t and ρ is the density of the adsorbent.

Moreover, the equilibrium adsorption equation must be considered; for example, if Langmuir equation is used, we get

$$\left(\frac{\partial n}{\partial t}\right)_z = n_{\mathrm{M}}\frac{k}{(k+c)^2}\left(\frac{\partial c}{\partial t}\right)_z \qquad (13)$$

and eq 12 becomes

$$n_M\frac{k}{(k+c)^2}\left(\frac{\partial c}{\partial t}\right)_z = \frac{3}{R}K(c_{\mathrm{s}} - c) \qquad (14)$$

To solve the previous set of differential equations, the following boundary and initial conditions can be utilized:

$$\text{Initial Condition} \qquad t = 0 \qquad 0 \le z \le L \qquad c_i = 0 \qquad (15)$$

$$\text{Boundary Condition} \qquad t > 0 \qquad z = 0 \qquad c_i = c_i^{\mathrm{in}} \qquad (16)$$

where L represents the bed length and c_i^{in} the concentration of the i solute in the feed.

The set of differential and algebraic equations can be solved by using gPROMS,[14] a general-purpose modeling package capable of describing the dynamic response of an unsteady-state apparatus. A backward finite-difference method was selected in order to discretize the spatial domain and obtain a set of time dependent differential and algebraic equations (DAEs).

The concentration of the solute in the vapor and the solid phase at different z and t values can be obtained by integrating the above DAE set once bed properties, fluid velocity, and overall mass transfer coefficient are fixed.

In this work, the K coefficient was considered as an adjustable parameter to be determined from the correlation of experimental data. To this aim, experimental breakthrough curves were compared with the values of solute concentration in the vapor phase at $z = L$, calculated by integration of the above DAE set. In particular, the following objective function was defined:

$$\Phi = \sum_{k=1}^{n_k}\sum_{m=1}^{n_m}(c_{\mathrm{k}}^{\exp}(t_{\mathrm{m}},L) - c_k^{\mathrm{calc}}(t_m,L))^2 \qquad (17)$$

where n_k represents the number of breakthrough curves experimentally measured for each solute ($n_k = 5$ both for MTBE and for 1-methylbutane) and n_m represents the number of experimental data for each curve. The values of K for the systems MTBE + air and 1-methylbutane + air obtained from the minimization of the objective function (eq 17) are equal to 9.987×10^{-3} and 5.023×10^{-3} $\mathrm{m \cdot s^{-1}}$, respectively. In Figure 2 a comparison between experimental breakthrough curves and theoretical ones calculated by means of the model is reported. The fit is quite satisfactory for different values of inlet solute concentration. It must be pointed out that the K values indicate that the MTBE adsorption is faster than that of 1-methylbutane.

Kinetics of Multisolute Mixtures. The same differential balance equations can be utilized in the case of a multisolute adsorption process. Obviously, it is possible to write the eqs 11 and 12 for each solute:

$$\nu\left(\frac{\partial c_i}{\partial z}\right)_t + \epsilon\left(\frac{\partial c_i}{\partial t}\right)_z + (1-\epsilon)\frac{3}{R}K_i(c_i - c_{i,\mathrm{s}}) = 0 \qquad (18)$$

$$\rho\left(\frac{\partial n_i}{\partial t}\right)_z = \frac{3}{R}K_i(c_{i,\mathrm{s}} - c_i) \qquad (19)$$

Furthermore, the equilibrium condition must be considered:

$$n_i = F(c_{i,\mathrm{s}}) \qquad (20)$$

It must be pointed out that, in the case of a multisolute mixture, the adsorption capacity for each solute depends on the concentrations of all solutes, as shown in the previous paragraph dealing with correlation of multisolute equilibrium data. In this work the equilibrium condition is expressed by means of the IAS model.

The theoretical breakthrough curves for mixtures of MTBE + 1-methylbutane + air were calculated by solving the obtained DAE set by gPROMS, assuming the operating conditions were equal to those of experimental data and by imposing, for each solute, boundary and initial conditions equal to those reported in eqs 15 and 16. It is worth noting that, in the present work, mass transfer coefficients K_i were assumed constant for each solute: therefore, K_i values obtained from fitting of single solute solutions can be utilized also in eqs 18 and 19. In other words, the model is fully predictive for the multisolute solution adsorption.

Theoretical and experimental breakthrough curves are presented in Figure 3 for two values of initial MTBE and 1-methylbutane solute concentrations: Figure 3A refers to initial concentrations equal to (37 and 71) $\mathrm{mg \cdot L^{-1}}$, and Figure 3B refers to initial concentrations equal to (84 and 71) $\mathrm{mg \cdot L^{-1}}$. The level of agreement appears quite satisfactory, especially in view of the fact that the model is completely predictive for multisolute adsorption. Furthermore, the model makes a correct estimation of the 1-methylbutane concentration profile: the model predicts the increase in 1-methylbutane outlet concentration caused by the displacement of 1-methylbutane from MTBE. Because of that displacement, the "maximum excess concentration" phenomenon that always appears in the adsorption beds when solutes show different adsorption kinetics can be observed. The model also predicts a regular trend of the MTBE profile, with a progressive saturation of the adsorbing bed from the inlet to the outlet section.

Therefore, the model can be used to make a correct estimation of the capacity of activated carbon to adsorb vapors of MTBE and 1-methylbutane under different operating conditions or conversely to predict, for mixtures of MTBE + 1-methylbutane + air at given concentrations, the decontamination level that can be achieved with a given activated carbon amount.

Conclusions

The present work reports theoretical and experimental information useful to study the feasibility of an adsorption process to treat an air stream containing MTBE and 1-methylbutane. This specific mixture was considered in order to simulate the streams arising from gasoline tanks of motor cars. All hydrocarbon vapors are lumped into 1-methylbutane whereas MTBE was individually considered because of its high environmental impact. In particular, breakthrough curves were obtained for bisolute mixtures of MTBE + 1-methylbutane + air and for single solute mixtures (MTBE + air and 1-methylbutane + air), with the aim to obtain information on equilibrium and kinetic phenomena.

Activated carbon shows a high adsorption capacity for both solutes considered in this work. In particular, maximum adsorption capacities for MTBE and 1-methylbutane equal to about 0.55 and 0.45, respectively, were obtained. These values agree with the few data reported in the literature.

MTBE adsorption capacity is strongly reduced in the presence of 1-methylbutane. This effect must be taken into consideration in modeling an adsorption process devoted to the treatment of air streams containing organic vapors and MTBE. This compound is the most hazardous one, and therefore process operating conditions must be chosen in such a way that standard requirements for MTBE can be achieved.

A theoretical model, based only on single solute solution data, can be used to predict the equilibrium behavior of the MTBE + 1-methylbutane + air system.

Experimental breakthrough curves of single solute solutions show that the adsorption rate can be described in terms of an overall mass transfer coefficient (K) from the gas to the adsorbed phase. The values of K obtained by fitting of experimental data show that MTBE adsorbs faster than 1-methylbutane onto activated carbon.

The competitive effect between MTBE and 1-methylbutane is evident from the analysis of breakthrough curves of MTBE + 1-methylbutane mixtures + air. In particular, 1-methylbutane shows a maximum excess concentration caused by the displacement of adsorbed 1-methylbutane by MTBE.

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