Adsorption of Halogenated Hydrocarbons from Gaseous Streams by Amberlite XAD-4 Resin and Activated Carbon: Equilibria

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Single-solute adsorption equilibria have been measured for the adsorption of the gaseous solutes chloroform, chlorobenzene, and 1,1,1-trichloroethane onto Amberlite XAD-4 resin. For 1,1,1-trichloroethane the adsorption equilibrium has also been measured with activated carbon Norit ROW 0.8 SUPRA as a sorbent. Temperature was varied between 20 and 120 °C, whereas nitrogen was used as a dilutant. All obtained experimental data could be fitted satisfactorily with two different temperature dependent Freundlich equations, one derived by Halsey (1952) and another derived in this work. Adsorption of the halogenated hydrocarbons onto Amberlite XAD-4 as well as Norit ROW 0.8 SUPRA proved to be completely reversible. The adsorption capacity of Amberlite XAD-4 was found to decrease exponentially with increasing temperature, whereas the capacity of Norit ROW 0.8 SUPRA decreased in a linear way and at a much lower rate, reflecting the bad regeneration characteristics of activated carbon sorbents.The obtained data for the adsorption of gaseous chloroform and 1,1,1-trichloroethane onto Amberlite XAD-4 resin agreed surprisingly well with data that were earlier obtained with these same hydrocarbons being adsorbed from water, in which they were dissolved, by nonwetted Amberlite XAD-4 particles. When plotted against the partial pressure of the solutes, equal adsorption capacities were found, indicating that, at least at 20 °C, the presence of water vapor inside the pores of the nonwetted resin particles does not affect the adsorption capacity of these particles with respect to the halogenated hydrocarbons in concern.

Introduction

A large number of water treatment methodologies is available nowadays. Adsorption on activated carbon is one of the most frequently applied techniques for the removal of trace pollutants. Though this technique has proved to be broadly applicable, an important disadvantage is the inability of activated carbon to desorb any adsorbed components completely (Kennedy, 1973; Cornel, 1986).

In the early 60s synthetic sorbents became available that can be easily regenerated by acids, bases, or organic solvents but also by hot gases or steam at moderate temperatures, which makes on-site regeneration a technically and economically attractive option (Gustafson et al., 1968). Especially regeneration with steam is very effective, since the desorbed solute can be easily recovered in pure form through phase separation after condensation of the steam. When the loaded sorbent is to be regenerated using low-pressure steam, the temperature of the sorbent rises from 20 to above 100 °C, causing the solute to desorb in a gaseous environment.

To determine the thermal regenerability of a sorbent, its adsorption capacity should be known as a function of temperature. However, data on adsorption equilibria at elevated temperatures are relatively scarce. In this paper gas-phase adsorption equilibria at temperatures between 20 and 120 °C are presented for the sorption of chloroform, chlorobenzene, and 1,1,1-trichloroethane by Amberlite XAD-4 resin as well as for the sorption of 1,1,1-trichloroethane on Norit ROW 0.8 SUPRA activated carbon.

Theory

For nearly all synthetic polymer sorbents, the isosteric enthalpy of adsorption decreases logarithmically with surface coverage. Halsey (1952) has shown that the adsorption capacity of sorbents showing such behavior can be well described by the Freundlich isotherm, although its thermodynamic consistency at zero coverage remains questionable, as the heat of adsorption then takes an infinite value. The Freundlich isotherm is expressed by

$$q = K_F^g \, p_s^{1/n_F} \tag{1}$$

where p_s is the partial pressure of the solute, q is the sorbent loading, and K_F^g and n_F are characteristic constants that depend on temperature, type of sorbent, and type of solute.

Halsey (1952) derived a Freundlich equation with an explicit relation for the influence of temperature for adsorption from the gas phase:

$$q = q_{mono}\left(\frac{p_s}{p_s^{vap}}\right)^{kT/\chi_m(1-rT)} \tag{2}$$

where p_s^{vap} is the vapor pressure of the solute, q_{mono} is the sorbent loading at $p_s/p_s^{vap} = 1$, k is the Boltzmann constant, T is the temperature, χ_m is the average adsorption enthalpy of the adsorption sites, and r is a constant. Below, a somewhat different approach is applied to obtain a

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Table 1. Boiling Temperature t_{boil}, Molar Mass *M*, Activity Coefficient at Infinite Dilution γ^{∞}, and Other Properties of Applied Hydrocarbons at 20 °C

name	purity/mass %	$t_{boil}{}^{a}$/°C	M^{a}/kg mol^{-1}	vapor pressure^{b}/kPa	density^{a}/kg m^{-3}	$\gamma^{\infty\ c}$
1,1,1-trichloroethane	>99	74	0.1335	10.10	1339	5595
chloroform	>99	61	0.1195	20.94	1480	802
chlorobenzene	>99	132	0.1126	1.20	1106	3000

[a] Weast (1983). [b] Yaws (1994). [c] Averaged data from Gmehling (1994).

comparable expression. As stated above, sorbents displaying Freundlich type adsorption show a logarithmic dependency of the isosteric adsorption enthalpy ΔH_{st} on sorbent loading:

$$-\Delta H_{st} = \alpha \ln q + \beta \tag{3}$$

with α and β being characteristic constants depending on type of solute and sorbent. The isosteric adsorption enthalpy can be determined from experiments using the van't Hoff equation, which expresses how solute activity changes with temperature at constant pressure and constant sorbent loading (Parfitt, 1983):

$$-\Delta H_{st} = RT^2\left(\frac{\mathrm{d}\ln p_s}{\mathrm{d}T}\right)_{P,q} \tag{4}$$

with p_s representing solute partial pressure. Integrating eq 4 yields

$$p_s(T) = p_s(T_0)\mathrm{e}^{(-\Delta H_{ads}/R)[(1/T_0)-(1/T)]} \tag{5}$$

Substituting eqs 1 and 3 into eq 5 results in

$$p_s(T) = \left(\frac{q}{K_F^{g,0}}\right)^{n_F^0} \mathrm{e}^{[(\alpha \ln q+\beta)/R][(1/T_0)-(1/T)]} \tag{6}$$

where n_F^0 and $K_F^{g,0}$ are the Freundlich constants at the reference temperature T_0. Rearranging eq 6 into a form similar to eq 1 yields

$$q = \exp\frac{n_F^0 \ln K_F^{g,0} - \dfrac{\beta}{R}\left(\dfrac{1}{T_0}-\dfrac{1}{T}\right)}{n_F^0 + \dfrac{\alpha}{R}\left(\dfrac{1}{T_0}-\dfrac{1}{T}\right)} p_s^{[n_F^0+\alpha/R(1/T_0-1/T)]} \tag{7}$$

which is basically identical to eq 2 when the Antoine equation is substituted for p_s^{vap}.

Experimental Section

Materials. Relevant physical properties of the applied chlorinated hydrocarbons (obtained from Merck) are presented in Table 1. The relevant physical properties of the investigated sorbents have been given by Rexwinkel et al. (1999). If the sorbent is not wetted after 1 day of contact with distilled water, it is referred to as hydrophobic; otherwise, it is regarded to be hydrophilic. Amberlite XAD-4 resin consists of a macroreticular polystyrene−divinylbenzene copolymer. It may be considered to be composed of a large number of microspheres with diameters ranging from 30 Å to 1000 Å (Gustafson et al., 1968). The resin particles had a spherical shape, whereas the activated carbon particles had a cylindrical shape. Prior to use, both sorbents were pretreated to remove any impurities using the method described by Rexwinkel et al. (1999).

Adsorption Experiments. Adsorption capacity was measured by means of thermogravimetric analysis. A simplified flow scheme of the applied experimental setup is shown in Figure 1. The thermogravimetric analyzer (TGA) was of the Setaram TG85 type. The sorbent samples (150−500 mg) were kept in a small cup (i.d. = 8 mm) made out of stainless steel small-mesh wire-netting, which hung on a platinum wire inside a quartz tube (i.d. = 15 mm). The tube was placed in an oven which could be operated at temperatures between 20 and 1000 °C. The sample temperature was measured by a thermocouple placed directly underneath the sample cup.

The TGA was connected to a computer for data acquisition purposes. The gas mixture, which consisted of nitrogen and the halogenated hydrocarbon vapor in concern, was composed with the help of electronic mass flow controllers. A stream of nitrogen (0−80 mL(STP)/min) was saturated with halogenated hydrocarbon by leading it through a saturator containing the liquid halogenated hydrocarbon which was kept at a constant temperature. Condensation of the hydrocarbon vapor in the supply lines was prevented by tracing. The saturated stream was mixed with a second nitrogen stream (0−400 mL(STP)/min) and then directed downward through the TGA. The nitrogen gas was taken from bottles and had a purity of 99.999%. To protect the upper section of the TGA, containing the delicate electronic parts of the balance, a small nitrogen stream (40 mL(STP)/min) was applied for purging.

Before starting an experiment, the sorbent sample was kept at 120 °C while purging with pure nitrogen for 2 h in order to remove any adsorbed components. Subsequently, the mixture of halogenated hydrocarbon and nitrogen was sent to the TGA. First, the sorbent sample was allowed to reach equilibrium at 120 °C. When no substantial change in sorbent sample weight was measured during 1 h, it was assumed that equilibrium had been reached. Subsequently, the temperature of the sorbent particles was decreased to 20 °C, using various cooling rates. At 20 °C the sample temperature was kept constant for 1 h and subsequently raised again to 120 °C using various heating rates. The weight and temperature of the sorbent sample were continuously monitored.

Results and Discussion

Adsorption of Halogenated Hydrocarbons by Amberlite XAD-4. The results of a typical gas-phase adsorption experiment are shown in Figure 2. The weight lost by the sample, after 2 h of purging with a pure nitrogen stream at 120 °C, was less than 0.5 mass %. Subsequently, the sample weight immediately started to increase when the sorbent came into contact with the mixture of chlorobenzene and nitrogen. After about 1 h the weight stabilized, indicating that the adsorption equilibrium was attained. Next, the temperature was decreased from 120 to 20 °C at a rate of 0.03 °C/min, causing the sample weight to increase due to adsorption of the solute. Then, after having kept the sample at 20 °C for 60 min, the temperature was raised again to 120 °C at a rate of 0.03 °C/min. It has been confirmed experimentally that buoyancy effects had negligible influence on the results.

When both the temperature and weight of a sample remain constant, sorbent and gas are at equilibrium.

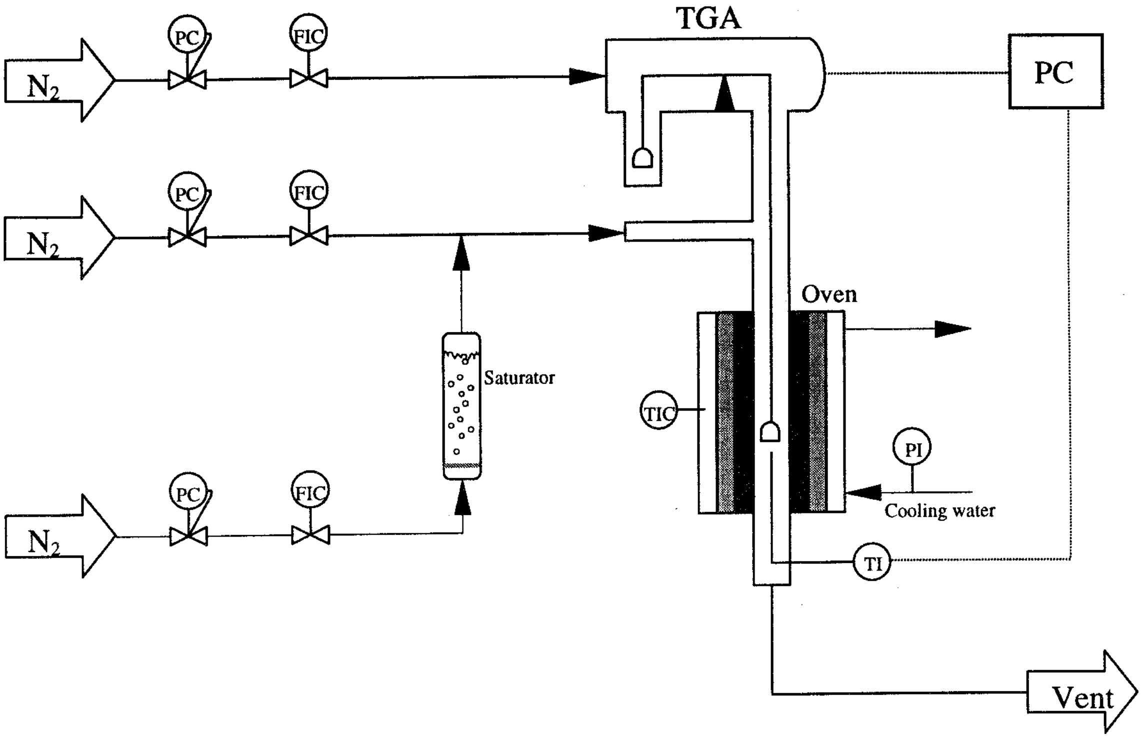

Figure 1. Simplified flow scheme of the applied experimental setup.

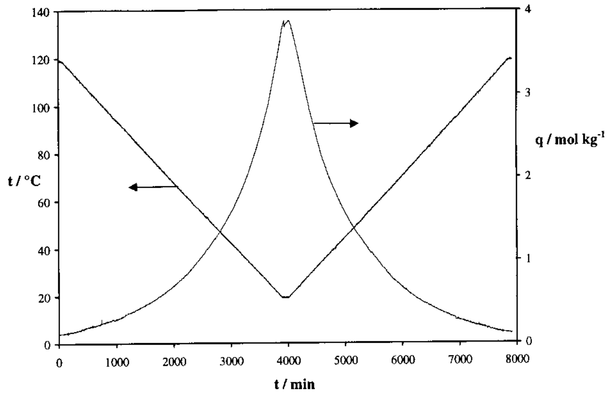

Figure 2. Typical gas-phase adsorption experiment. Adsorption of chlorobenzene onto Amberlite XAD-4. Heating and cooling rate: 0.03 °C/min. p_s = 149.3 Pa. Sample mass: 125 mg.

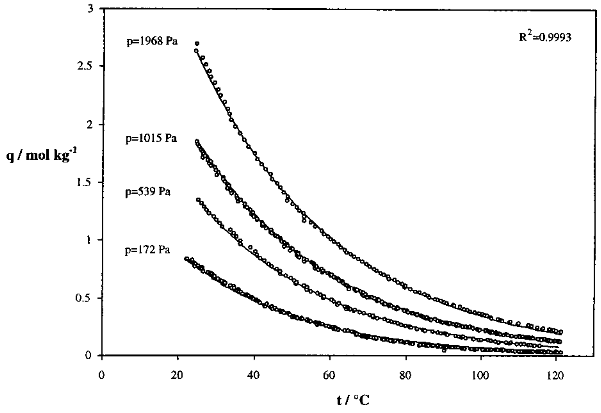

Figure 3. Adsorption capacity of Amberlite XAD-4 resin for 1,1,1-trichloroethane as a function of partial pressure and temperature. The dots represent measured sorbent loading, whereas the solid lines represent fits using eq 2 with $\chi_m = 1.02 \times 10^{-20}$ J, $r = 6.65 \times 10^{-4}$ K^{-1}, and q_{mono} = 6.55 mol/kg. Sample mass = 150 mg.

However, when temperature is changing, equilibrium is continuously disturbed and mass-transport phenomena may become of interest. Outside the sorbent particles solute material must be supplied by film diffusion and convection, whereas inside the particles transport must take place through Knudsen and surface diffusion. When the cooling rate is too high, mass transfer will limit the rate of adsorption and the adsorption capacity will be underestimated. On the other hand, when the heating rate is too high, the adsorption capacity will be overestimated.

It appeared that, in the case of 1,1,1-trichloroethane and chloroform, a heating/cooling rate of 0.2 °C/min was low enough to keep equilibrium established. With chlorobenzene, much lower partial pressures were applied and the heating/cooling rate had to be as low as 0.03 °C/min to maintain equilibrium. The results of 1,1,1-trichloroethane adsorption onto Amberlite XAD-4 are shown in Figure 3. It was tried to fit these results with the Freundlich equation derived by Halsey (1952), as represented by eq 2. This equation fits the experimental data very well, considering the correlation coefficient R^2 being as high as 0.9993. Solute vapor pressure was calculated as a function of temperature using the correlation proposed by Yaws (1994). Also, the temperature dependent Freundlich equation derived in this work, which is represented by eq 7, is capable of fitting the measured data equally well, as is illustrated by the parity plot in Figure 4.

Equations 2 and 7 also fit the results obtained for the adsorption of chloroform and chlorobenzene onto Amberlite XAD-4 very well. Table 2 summarizes the experimental conditions and the best-fit values of the constants used in eq 2 and 7.

After an experiment was completed, the TGA was purged again with pure nitrogen gas while keeping the sample at 120 °C. In all cases the sample weight returned to its initial value, indicating that adsorption of the applied hydrocarbons onto Amberlite XAD-4 is completely reversible.

Adsorption of 1,1,1-Trichloroethane by Norit ROW 0.8 SUPRA. The adsorption equilibrium of 1,1,1-trichlo-

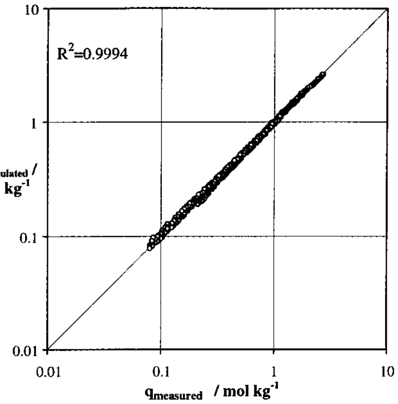

Figure 4. Parity plot of measured and calculated adsorption capacity of Amberlite XAD-4 resin for 1,1,1-trichloroethane. Temperature ranges from 20 to 120 °C; partial solute pressure from 172 to 1968 Pa. Calculated capacities were obtained with eq 7 with $T_0 = 273$ K, $\alpha = -5295$ J/mol, $\beta = 43994$ J/mol, $n_F^0 = 2.18$, and $K_F^0 = 0.154$. Sample mass = 150 mg.

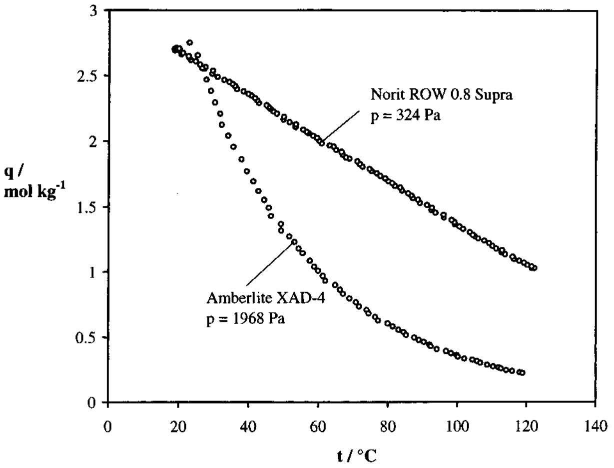

Figure 5. Adsorption equilibrium of 1,1,1-trichloroethane onto Amberlite XAD-4 and Norit ROW 0.8 SUPRA as a function of temperature.

roethane onto Norit ROW 0.8 SUPRA has been measured at four different partial pressures varying from 193 to 3146 Pa and at temperatures between 20 and 120 °C. The result of one experiment is included in Figure 5 together with a result obtained with Amberlite XAD-4. Whereas the adsorption capacity of Amberlite XAD-4 decreases exponentially with increasing temperature, the capacity of Norit ROW 0.8 SUPRA decreases almost linearly and at a much slower rate.

After purging with pure nitrogen at 120 °C, the sample weight returned to its initial value. So, also in the case of adsorption of 1,1,1-trichloroethane onto Norit ROW 0.8 SUPRA, adsorption is completely reversible. Apparently, the bad thermal regeneration characteristics of activated carbon, which are frequently reported in the literature, are not necessarily the result of the irreversibility of adsorption but may also be caused by the moderate influence of temperature on the adsorption equilibrium.

Though the fits according to eqs 2 and 7 are reasonable, they are not as good as those with Amberlite XAD-4. In Table 2 the experimental conditions and the obtained best-fit values of the constants applied in eqs 2 and 7 are presented.

Water- and Gas-Phase Equilibria with Nonwetted Amberlite XAD-4: A Comparison. Adsorption of 1,1,1-trichloroethane and chloroform from an aqueous solution onto nonwetted Amberlite XAD-4 resin has been investigated earlier by Rexwinkel et al. (1999). The pores of the applied nonwetted Amberlite XAD-4 resin particles were filled with gas, and adsorption actually took place in the gas phase. By comparing the data obtained by Rexwinkel et al. (1999) with the data reported here, the influence of the presence of water vapor in the pores can be determined.

To do so, we calculate the partial pressure of the water dissolved solute inside the sorbent pores by using Raoult's law:

$$p_s = \gamma \chi p_s^{vap}$$

where x is the mole fraction of solute in solution and γ is the activity coefficient. At low solute concentrations eq 8 can be written as

$$p_s = \gamma^{\infty} \frac{c_l M_w}{\rho_w} p_s^{vap}$$

where γ^{∞} is the activity coefficient at infinite dilution, c_l is the solute concentration, M_w is the molar mass of water, and ρ_w is the water density. We now can compare the results of the water-phase experiments with the gas-phase results reported here. In Figure 6. water-phase data are plotted versus the solute partial pressure, as calculated

Table 2. Experimental Conditions for the Adsorption Experiments with Amberlite XAD-4 and Norit ROW 0.8 SUPRA and the Best-Fit Values of the Constants Used in eqs 2 and 7

solute sorbent	1,1,1-trichloroethane Amberlite XAD-4	chloroform Amberlite XAD-4	chlorobenzene Amberlite XAD-4	1,1,1-trichloroethane Norit ROW 0.8 SUPRA
Experimental Conditions				
temp range/°C	20−120	20−120	20−120	20−120
partial pressure range/Pa	172−1968	317−2408	16.9−149.3	193−3146
sorbent mass/g	0.15	0.15	0.125	0.50
heating and cooling rate/°C min^{-1}	0.2	0.2	0.03	0.25
Constants for Eq 2				
R^2	0.9993	0.9992	0.9956	0.9912
q_{mono}/mol kg^{-1}	6.55	9.18	8.85	4.32
r/K^{-1}	6.65×10^{-4}	4.31×10^{-4}	8.27×10^{-4}	1.12×10^{-3}
χ_m/J	1.02×10^{-20}	8.88×10^{-21}	1.14×10^{-20}	4.68×10^{-20}
Constants for Eq 7				
R^2	0.9994	0.9992	0.9966	0.9960
T_0/K	273	273	273	273
α/J mol^{-1}	−5295	−4945	−5597	−42189
β/J mol^{-1}	43994	43372	55896	76944
n_F^0	2.18	2.07	2.28	9.56
$K_F^{g,0}$	0.154	0.119	0.731	1.62

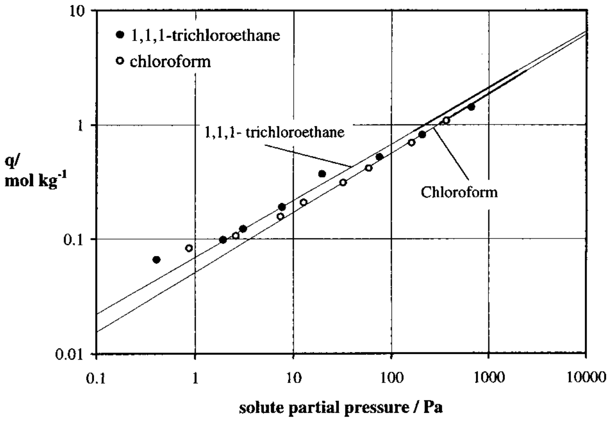

Figure 6. Water-phase equilibrium loadings of 1,1,1-trichloroethane and chloroform onto Amberlite XAD-4 resin at 20 °C versus partial pressure of the gaseous solute inside the sorbent pores. The solid lines represent the gas-phase adsorption isotherms that were measured in this work, whereas the dotted lines are extrapolations of these measurements, using eq 7 and the best-fit values of Table 2.

with eq 9 for a temperature of 20 °C, which was applied by Rexwinkel et al. (1999).

The adsorption isotherms obtained in the gas- and water-phase experiments do not differ significantly, indicating that, at least at 20 °C, the presence of water vapor inside the resin pores does not decrease the adsorption capacity of nonwetted Amberlite XAD-4 resin with respect to both halogenated hydrocarbons. This result suggests that the adsorption capacity of nonwetted Amberlite XAD-4 for a water-dissolved apolar solute can be predicted from gas-phase measurements in combination with Raoult's law.

Conclusions

Adsorption of gaseous 1,1,1-trichloroethane, chloroform, and chlorobenzene onto Amberlite XAD-4 as well as adsorption of 1,1,1-trichloroethane onto Norit ROW 0.8 SUPRA has been examined at temperatures between 20 and 120 °C. The obtained results could be fitted satisfactorily using the temperature dependent Freundlich equation derived by Halsey (1952) but also with a somewhat different equation derived in this work. The adsorption capacity of Amberlite XAD-4 was found to decrease exponentially with increasing temperature, whereas the adsorption capacity of Norit ROW 0.8 SUPRA was found to be much less dependent on temperature. Adsorption of all applied halogenated hydrocarbons onto both Amberlite XAD-4 and Norit ROW 0.8 SUPRA proved to be completely reversible.

The results obtained with 1,1,1-trichloroethane and chloroform in combination with Amberlite XAD-4 resin were found to compare quite well with data that were derived from earlier experiments in which water dissolved 1,1,1-trichloroethane and chloroform was adsorbed on nonwetted Amberlite XAD-4 particles. It is therefore concluded that, at least at 20 °C, the presence of water vapor inside the pores of nonwetted particles does not affect the adsorption capacity with respect to the apolar hydrocarbons in concern. This is consistent with earlier results obtained by Rexwinkel et al. (1999) which showed no significant difference in adsorption equilibrium between wetted and nonwetted Amberlite XAD-4 resin.

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