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An Extended Equation for Rate Coefficients for Adsorption of Organic Vapors and Gases on Activated Carbons in Air-Purifying Respirator Cartridges

Organic vapor adsorption rates in air-purifying respirator cartridges (and other packed beds of activated carbon granules) need to be known for estimating service lives. The correlation of Lodewyckx and Vansant [*AIHAJ 61*:501–505 (2000)] for mass transfer coefficients for organic vapor adsorption onto activated carbon was tested with additional data from three sources. It was then extended to better describe all the data, including that for gases. The additional parameter that accomplished this was the square root of molar equilibrium capacity of the vapor or gas on the carbon. This change, along with skew corrections when appropriate, resulted in better correlations with all experimental rate coefficients.

Keywords: activated carbon, adsorption, cartridges, kinetics, organic vapors, respirators

Most air-purifying respirator cartridges for organic vapors contain packed beds of activated carbon granules. Adsorption rate from flowing air is one of the parameters, which determine such bed (and cartridge) breakthrough times (service lives) by vapors and gases. Other parameters include gas/vapor properties, adsorption capacity, carbon properties, bed geometry, and use conditions, such as relative humidity (RH), temperature, airflow rate, and vapor concentrations.

As part of an effort to develop improved equations for estimating bed breakthrough times (service lives), the objective of the work reported here was to test and improve existing equations for predicting adsorption rate coefficients.

BACKGROUND

A variety of equation models[(1–11)] have been proposed to predict adsorption rate coefficients k_v for the Wheeler-Jonas equation or for its reaction kinetic form:

$$t_b = \frac{W_e W}{C_o Q} - \frac{W_e \rho_B}{k_v C_o} \ln\left(\frac{C_o - C_x}{C_x}\right), \qquad (1)$$

where t_b (min) is the breakthrough time, C_o (g/cm^3) is the challenge vapor concentration, C_x is the breakthrough concentration, W_e (g/g carbon) is the gravimetric capacity, W (g) is the weight of carbon, Q (cm^3/min) is the volumetric airflow rate, and ρ_B (g/cm^3) is the packed density of the carbon bed. In a review[(12)] of these models, only the Wood/Stampfer[(10)] and Lodewyckx/Vansant[(11)] models showed positive correlations with experimental rate coefficients for a wide variety of chemical vapors.

The empirical Wood/Stampfer model[(10)] uses molar polarizability (P_e in cm^3/mol) as the parameter to account for different adsorption rates for different chemicals. It also takes into account linear flow velocity (v_L in cm/sec):

$$k_v = [(v_L^{-1} + 0.027)(I + S_b/P_e)]^{-1} \text{ min}^{-1} \qquad \textbf{(2)}$$

for I=0.000825 min (cm/sec) and $S_b = 0.063 - 0.0055 \ln[(C_o - C_x)/C_x]$. This model has the advantage of incorporating skew (breakthrough curve asymmetry) to account for observations of differing rate coefficients calculated at differing breakthrough concentration fractions C_x/C_o.[(10,13)]

A more thorough examination of skew effects was more recently completed.[(14)] One application of this skew analysis is to estimate an adsorption rate coefficient at a desired breakthrough fraction from one known at another breakthrough fraction. A skew parameter defined as:

$$S = k_{v1\%}/k_{v10\%} = [a + ab\ \ln(99)]/[a + ab\ \ln(9)] \tag{3}$$

was found to correlate with the data as:

$$S = 1.41 - 0.0000324\left[\frac{1 + b\ \ln(9)}{1 + b\ \ln([C_o - C_x]/C_x)}\right]k_{v(C_x/C_o)} \tag{4}$$

with a lower limit of S=1. From an experimental or calculated $k_{v(Cx/Co)}$ one can solve Equations 3 and 4 for "a" and "b" and calculate a rate coefficient

$$k_{v(C_x/C_o)} = a\left[1 + b\ \ln\left(\frac{C_o - C_x}{C_x}\right)\right]\ \text{min}^{-1} \tag{5}$$

at another breakthrough fraction C_x/C_o.

The empirical Lodewyckx/Vansant equation[11] for rate coefficients was based on k_v calculated using (1) a rearranged Equation 1 with experimental times for 0.1% breakthrough and (2) independently calculated adsorption capacities W_e. The result includes affinity coefficient β, which is a function of the chemical:

$$k_v = 48\ \beta^{0.33}\ v_L^{\,0.75}\ d_p^{\,-1.5}\ \text{min}^{-1} \tag{6}$$

It has the advantages of also including average carbon granule diameter (d_p in centimeters) and linear flow velocity as parameters. All experiments on which Equation 6 was based were at 5 g/m³ vapor concentration.

EXPERIMENTAL DATA

The authors compiled databases of breakthrough curves and/or breakthrough times for varieties of chemicals, carbons, and testing conditions from four sources. The first source was from the published work of Lodewyckx and Vansant (LV),[11] plus additional experimental results of theirs not previously reported or used. The total 54 dry experiment conditions included 7 carbon types; 6 granule diameters (0.10–0.34 cm); 12 chemicals and corresponding equilibrium adsorption capacities (0.11–0.70 g/g carbon); 12 flow velocities (1.9–32.9 cm/sec); 4 bed diameters (4.4–14.9 cm); 5 bed weights (20–100 g); and 5 g/cm³ concentration.

The second database source was the work of Nelson and coworkers in the 1970s. They measured 618 vapor breakthrough curves for 121 chemicals and 3 types of activated carbons in commercial respirator cartridges at the Lawrence Livermore National Laboratory (LLNL). Test conditions, results, analyses, and conclusions from these were reported in a series of papers culminating in a summary.[1] Other variables included vapor concentration, airflow rate, number of cartridges (one or two) in parallel, preconditioning RH, and test RH. Nelson[15] provided one of the current authors with the original full experimental breakthrough curve data, test conditions, interpolations of 1 and 10% breakthrough times, and calculated curve geometric centroids (stoichiometric times and fractions) for the 618 curves. Theoretically, the stoichiometric times t_{sto} correspond to the first term of Equation 1, so this was used to calculate experimental adsorption capacities, W_e. From Nelson's data and using Equation 1, $k_{v1\%}$ and $k_{v10\%}$ for each breakthrough curve were also calculated by:

$$k_{v1\%} = \frac{\rho_B Q}{W}\left[\frac{t_{sto}\ln(99)}{t_{sto} - t_{1\%}}\right] \tag{7}$$

and the corresponding equation for $k_{v10\%}$ using $t_{10\%}$ and ln(9). Only rate coefficient results for 451 "dry" (both preconditioning and test RHs≤50%) experiments were used for the purposes of this article.

The third source was work done at the Los Alamos National Laboratory (LANL) in the 1980s, where J.F. Stampfer led a team that measured 305 breakthrough curves for 33 gases and vapors and beds of 2 types of carbons. Wood and Stampfer[10] reported average 1 and 10% rate coefficients obtained from 165 of these experiments with 27 compounds and 1 carbon (12–30 mesh ASC Whetlerite). Conditions for these were: 2 cm bed depth, 2.3 cm bed diameter, 4.55 g carbon, 3% relative humidity, 23°C, 740 cm/sec airflow velocity, and three concentrations (340, 680, and 1320 ppm). Details of the experimental procedure were published previously.[10]

Additional breakthrough experiments were done at LANL that also included another carbon (12–30 mesh ASZM-3T, a carbon impregnated with metal salts and with triethylenediamine, at 4.78 g/2 cm depth) and six more compounds (acetone, ethyl acetate, chloroform, diethyl ether, perfluorobutane, and perfluoro-2,3-epoxy-2-methylpentane). Test conditions also included 1–6 cm bed depths, 370 cm/sec flow velocity. Most (242, including the originally reported 165) experiments were done at dry (3% RH) preconditioning and testing conditions.

All these 242 LANL breakthrough curves have been reanalyzed. To get 1%, 10%, and stoichiometric breakthrough times by interpolation and extrapolation, the authors selected only those curves with data including 2 to 80% breakthroughs. Also, because rapidly eluting gases do not have time to form constant pattern wavefronts and there are no practical applications for rapidly eluting gases, only those curves with $t_{1\%}>2$ min were selected. Five of the C-2 and fluorinated C-2 gases were thereby eliminated. These selections left 183 useful breakthrough curves for 26 compounds. The authors fit each of these remaining breakthrough curves to an asymmetric breakthrough curve equation[13,14] using four experimental breakthrough times near 1, 10, 50, and 90% breakthrough fractions. The resulting four fit parameters allowed interpolation, extrapolation, and integration to get $t_{1\%}$, $t_{10\%}$, and t_{sto}. For each breakthrough curve a rate coefficient $k_{v1\%}$ was then calculated by Equation 7 and $k_{v10\%}$ by the corresponding one with $t_{10\%}$ and ln(9).

For the fourth source the authors used the work of Smoot et al.[16] of the Bendix Corp. (NASA), who published a literature review of adsorption equations. This report also included new experimental breakthrough time data for 12 organic liquids and a 12–20 mesh Witco petroleum-based activated carbon (Witcarb 337). Experimental conditions were 1000 ppm vapor concentration, 25°C, and 32 L/min airflow through a 7 cm diameter by 2.2 cm deep bed of packed density 0.40 g/cm³. Test RHs were 0, 50, and 80%. No preconditioning was mentioned, but similar listed values of starting carbon weights at each RH and positive water uptakes at 50 and 80% RHs imply that all the carbon samples were dry to start with.

Smoot reported at least duplicate experiments at each RH for each compound. The present authors analyzed 121 of the individual breakthrough experiments for which 1, 10, 50, and 90% breakthrough times were all reported. Again each of these breakthrough curves was fit to an asymmetric breakthrough curve equation[13] to get the stoichiometric time for calculating $k_{v1\%}$ by Equation 7 and $k_{v10\%}$ by the corresponding equation for 10% breakthrough. For the purposes of this article only the rate coefficients from 88 "dry" (0 or 50% test RH) breakthrough curves were used.

These four sources gave a total of 776 dry experimental rate

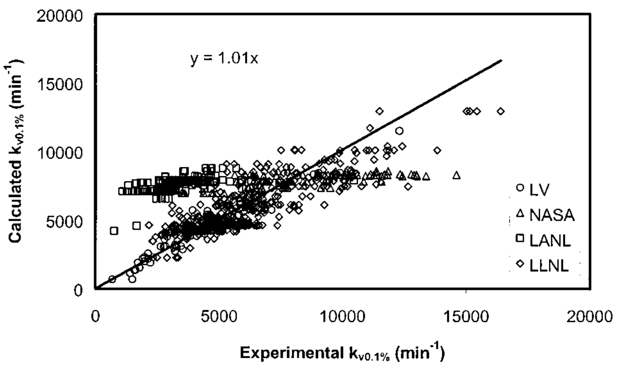

FIGURE 1. A comparison of predictions of the original LV rate coefficient Equation 6 with experimental values derived from four sources

coefficients to test equations for predicting adsorption rate coefficients.

PRELIMINARY RESULTS

The Lodewyckx-Vansant Equation 6 for adsorption rate coefficients was developed from data for 0.1% breakthrough fraction. The LLNL, LANL, and NASA experimental data, analyzed as described previously, yielded rate coefficients at the higher breakthrough fractions of 1 and 10%. Therefore, it was necessary to extrapolate the latter to 0.1% using the skew function(14) (Equations 3 and 5) for each breakthrough curve. These were then compared with Equation 6, using $\beta = 0.0862\ P_e^{0.75}$ for the affinity coefficients.(17)

Figure 1 shows the results of comparing 776 experimentally derived 0.1% adsorption rate coefficients from the four sources with predictions of the Lodewyckx-Vansant Equation 6. Overall accuracy (slope of 1.01) was good, but overall precision of this LV model was not (correlation coefficient=0.53). The major deviations from the calculated versus experimental equivalency line were with data from the LANL and NASA experiments.

Some of the deviations of NASA data can be explained by experimental variations, which can easily introduce errors into the calculation of rate coefficients from breakthrough times. For example, in Equation 7 small errors in t_{sto} and $t_{1\%}$ are propagated into larger errors in $k_{v1\%}$ as the difference between these two experimental times becomes smaller. This is apparently why, for example, $k_{v1\%}$ rate coefficients from seven carbon tetrachloride replicate experiments at dry/0% RH conditions varied from 4833 to 11,223 min^{-1}. The corresponding skew-extrapolated $k_{v0.1\%}$ rate coefficients varied from 6057 to 14,613 min^{-1}. Averages of these and replicates for other chemicals were closer to the equivalency line than were the extremes.

Not all deviations of the experimental data from Equation 6 could be attributed to such experimental variations. Therefore, the authors looked further for their explanations.

DISCUSSION

The LANL experiments were unique among these four sources in that they included chemicals that are gases at ordinary temperatures.(10) These gases also gave the smaller adsorption rate coefficients that deviated most from the LV model predictions (Figure 1). Gases are also known to have smaller adsorption capacities due to lower molecular polarizabilities and higher volatilities. This was a clue that a parameter might be missing from the LV correlation and that the parameter might be adsorption capacity. Because all the LV model basis data was measured at the same 5 g/m^3 vapor concentration, adsorption capacities of the test liquids would be expected to be similar.

Simple reaction kinetic mechanism analysis shows that adsorption rate should be a function of adsorption capacity. At gas/vapor A concentration [A] and low (compared with equilibrium) adsorbed concentration [AS] at adsorbent sites S, the desorption rate is negligible, so that the adsorption rate can be expressed as

$$\frac{d[AS]}{dt} = k_a[A][S] \tag{8}$$

where the brackets represent mole per liter units and k_a is the adsorption rate coefficient. Also at such low adsorbate levels,

$$[S] = [S]_o - [AS] \approx [S]_o \tag{9}$$

the total concentration of adsorption sites (or volumes) before adsorption. However, at an equilibrium, which can be expressed as A + S ↔ AS, the total adsorption rate

$$\begin{aligned}\frac{d[AS]'}{dt} &= k_a'[A]'[S] - k_d'[AS]' \\ &= k_a'[A]'[S]_o - k_a'[A]'[AS]' - k_d'[AS]' \end{aligned} \tag{10}$$

is zero. The prime superscripts refer to equilibrium conditions, and k_d is the desorption rate coefficient. Combining Equations 8–10 gives

$$\frac{d[AS]}{dt} = k_a[A]\left(1 - \frac{k_d'}{k_a'[A]'}\right)[AS]' \tag{11}$$

Therefore, the adsorption rate is predicted to be a function of the molar equilibrium adsorption capacity [AS]′.

The same conclusion can be reached using the Dubinin/Radushkevich equation for equilibrium adsorption capacity,(10) which can be expressed in molar units and this symbolism as:

$$[AS]' = [S]_o \exp\left[-\left(\frac{RT}{\beta E_o}\right)^2 \ln^2\left(\frac{[A]'_{sat}}{[A]'}\right)\right] \tag{12}$$

so that

$$\frac{d[AS]}{dt} = k_a[A][AS]' \exp\left[+\left(\frac{RT}{\beta E_o}\right)^2 \ln^2\left(\frac{[A]'_{sat}}{[A]'}\right)\right] \tag{13}$$

Again, the adsorption rate is predicted to be a function of the molar equilibrium capacity.

Extended Adsorption Rate Coefficient Correlation

The Lodewyckx/Vansant Equation 6, therefore, was extended to include the parameter of equilibrium molar capacity to an adjustable power:

$$k_v = a\beta^{0.33}\, v_L^{0.75}\, d_p^{-1.5}\, (W_e/M_w)^n \text{ min}^{-1} \tag{14}$$

for gravimetric capacities W_e (g/g carbon) and molecular weights M_w. The 776 experimental, skew-extrapolated, 0.1% rate coefficients described previously and plotted in Figure 1 were best fit to Equation 14 with n=0.5. The resulting comparison is shown in Figure 2. The overall correlation coefficient of the four sets of data improved to 0.86. The value of a=793 produced the best

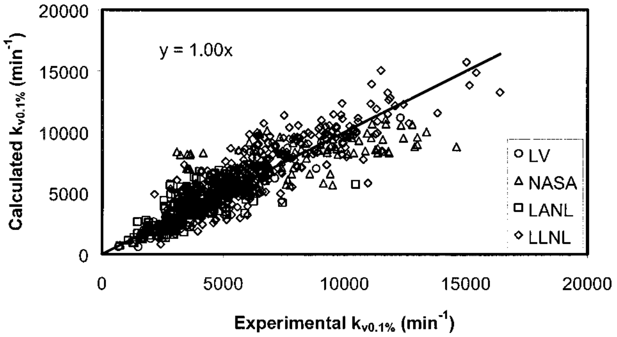

FIGURE 2. A comparison of predictions of the extended rate coefficient Equation 15 with experimental values derived from four sources

overall accuracy (best fit line slope of 1.00 in Figure 2). This value is essentially 800 within the uncertainties involved, so that:

$$k_{v0.1\%} = 800\ \beta^{0.33}\ v_L^{0.75}\ d_p^{-1.5}\ (W_e/M_w)^{0.5}\ \text{min}^{-1} \qquad \textbf{(15)}$$

The authors also tested this correlation with experimental rate coefficients that were not skew-extrapolated. Figure 3 shows how it predicts the 54 LV 0.1% rate coefficients obtained from experimental breakthrough times as described previously. The average model accuracy was 0.97, and the correlation coefficient was 0.96.

In another test, Equation 15 was skew-adjusted using Equations 3–5 to estimate 1% breakthrough rate coefficients $k_{v1\%}$ for the dry NASA, LLNL, and LANL experiments. Figure 4 shows comparisons of these estimates with 722 experimental, non-skew-extrapolated, 1% breakthrough rate coefficients. Again, the accuracy (1.00) and linear correlation coefficient (0.86) were good.

CONCLUSIONS

The new adsorption rate coefficient expression, Equation 15, provides an improved average description of experimentally derived rate coefficients for a wide variety of vapors or gases and conditions. It was developed from experiments at dry (RH≤50%) conditions and applies only to such. Effects of humidity and adsorbed water have been reported elsewhere.(12,18)

Equation 15 is also valid only for 0.1% breakthrough fraction.

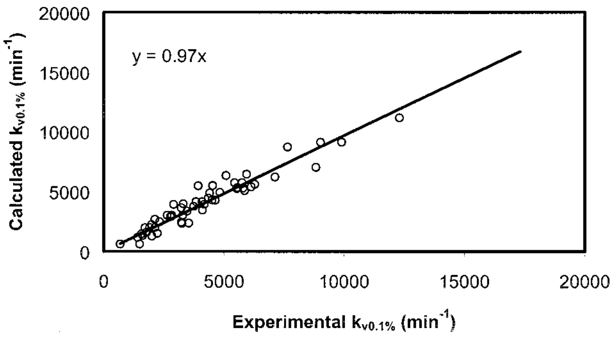

FIGURE 3. A comparison of predictions of the extended rate coefficient Equation 15 with experimental 0.1% rate coefficients from the work of Lodewyckx and Vansant

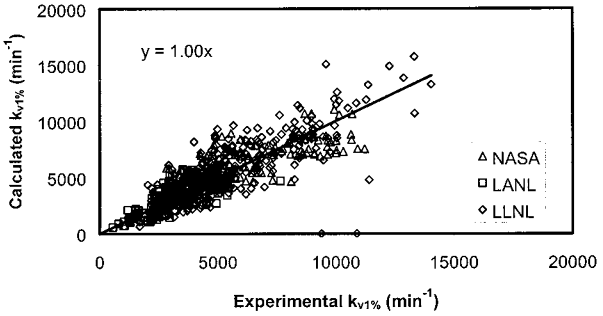

FIGURE 4. Predictions of the extended rate coefficient Equation 15, with skew corrections, compared with experimental 1% rate coefficients

However, the authors applied average skew parameters and functions to Equation 15 to successfully estimate adsorption rate coefficients at 1% breakthrough fraction. Therefore, such adjustments for breakthrough fraction extend the usefulness of Equation 15.

Although the correlations in Figures 2 and 4 are good, there is significant scatter around the calculated versus experimental equivalence lines. This can be attributed to experimental errors as much as to the best-fit model. A major source of such experimental errors is the method of extracting rate coefficients from breakthrough times (see the previous discussion concerning the NASA data).

The constant a=800 in Equation 15 may contain other parameters, such as temperature. All of the experimental data used for its derivation were near normal ambient temperatures and pressures (0.77 atm is normal at LANL). Additional data is required to discover effects of temperature on adsorption rate coefficients. The effect of concentration is not apparent in the data but is included in Equation 15 in the gravimetric capacity parameter W_e, which for a given carbon-vapor system is a function of vapor concentration as well as temperature.

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