Optimum Isotherm Equation and Thermodynamic Interpretation for Aqueous 1,1,2-Trichloroethene Adsorption Isotherms on Three Adsorbents

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Abstract. Aqueous 1,1,2-trichloroethene (TCE) adsorption isotherms were obtained on Ambersorb[1®] 563 and 572 adsorbents and Filtrasorb[2®] 400 granular activated carbon (GAC). The data for Ambersorb 563 adsorbent covers TCE concentrations from 0.0009 to 600 mg/L. The data for each adsorbent was fit to 15 isotherm equations to determine an optimum equation.

The best equation for the TCE adsorption isotherms is the Dubinin-Astakov (DA) isotherm. The DA isotherm coefficients were used to estimate the TCE micropore volume and the adsorption potential distribution. For each adsorbent, the TCE micropore volume is equivalent to the N_2 porosimetry micropore volume. The mean adsorption potential is 18.8, 13.0, and 8.9 kJ/mol, with coefficients of variation of 0.37, 0.53, and 0.67, for Ambersorb 563 and 572 adsorbents and Filtrasorb 400 GAC, respectively. Thus, Ambersorb 563 adsorbent has the most energetic and most homogeneous adsorption volume, while Filtrasorb 400 GAC has the least energetic and most heterogeneous adsorption volume. For these reasons, Ambersorb 563 adsorbent has the highest TCE capacity at low concentrations, whereas Filtrasorb 400 GAC has the highest TCE capacity at high concentrations. The performance of Ambersorb 572 adsorbent is generally intermediate to the other two adsorbents.

Keywords: adsorbent properties, liquid phase adsorption isotherms, activated carbon

1 Introduction

A. Background

The equilibrium performance of adsorbents at a constant temperature is given by the adsorption isotherm. An isotherm is the solid phase concentration of the adsorbed species as a function of the liquid phase concentration of that species at equilibrium. The isotherm depends on the adsorbent, the adsorbate or adsorbed species, and physical properties of the solution (temperature, pH, ionic strength, other species present, etc.) (Sontheimer et al., 1988a). Many different functions have been used in the literature to represent the isotherm.

A common adsorbent for removing contaminants from water is granular activated carbon (GAC). GACs are produced by the pyrolysis and activation of natural carbon containing materials such as peat, coke, bituminous coal, wood, and coconut shells. Several groups have published tables of GAC isotherm parameters for a

large number of organic chemicals (Dobbs and Cohen, 1980; Sontheimer et al., 1988b; Speth and Miltner, 1990). These groups used the Freundlich isotherm equation to represent their results. The Freundlich equation is a straight line when the isotherm is plotted on logarithmic axes.

The Rohm and Haas Company introduced the Ambersorb carbonaceous adsorbents in 1989. These synthetic adsorbents are manufactured by the partial pyrolysis of polysulfonated styrene-divinylbenzene ion exchange resins. Because of the synthetic nature of these adsorbents, they have properties significantly different from those of typical GACs.

Adsorption isotherms for the Ambersorb adsorbents are qualitatively different from those of typical GACs. First, the isotherms for Ambersorb adsorbents show significant curvature when plotted on logarithmic axes. Thus, the Freundlich equation cannot be used to represent these isotherms. Second, Ambersorb adsorbents have higher capacities at low concentrations, and lower capacities at high concentrations, than typical GACs.

Table 1.   Suitability of isotherm functions.

Isotherm	# Coef.	+Slope	Henry @ Low C	Finite @ High C	$q = F(C)$	$C = F(q)$
Freundlich	2	✓			✓	✓
Langmuir	2	✓	✓	✓	✓	✓
BET	2	✓	✓	✓	✓	✓
Myers	3		✓			✓
RP	3	✓	✓		✓	
2nd Ln Poly	3				✓	✓
DA	3	✓		✓	✓	✓
Toth	3	✓	✓	✓	✓	✓
HK	3	✓		✓	✓	✓
MJ	4	✓		✓	✓	✓
EI-1	2	✓		✓	✓	✓
EI-2	3			✓	✓	✓
EI-3	4			✓	✓	
EI-4	5			✓	✓	
EI-5	6			✓	✓	

A detailed study was performed on the adsorption isotherm of a typical GAC and two Ambersorb adsorbents. The primary objectives were to determine the "optimum" function for representing the isotherm data and to determine a thermodynamic explanation for the observed differences in the isotherm behavior.

B.   Criteria

The choice of an optimum isotherm function is somewhat subjective. The following criteria were used in this evaluation.

The first criterion is that the isotherm function must provide a good fit to the data. The quality of the fit is judged by the reduced chi-square statistic, χ^2/ν (Bevington, 1969a). This statistic is the variance of the fit divided by the average variance of the data. Thus, if the fitting function is a good approximation to the actual function, the value of the reduced chi-square statistic should be less than unity, i.e., $\chi^2/\nu \leq 1$ for a good fit. Larger values are indicative either of a poor fit or of scatter in the data greater than that expected based on the experimental error bars.

The second criterion is that the isotherm function should be thermodynamically realistic (Derylo-Marczewska and Jaroniec, 1987). The isotherm function should ideally meet three requirements: A) a linear isotherm as the concentration approaches 0, B) a finite capacity as the concentration approaches the maximum, and C) a positive slope for all concentrations. The first requirement is Henry's law. The second requirement reflects the finite surface area and pore volume for adsorption. Some isotherm functions, notably the Freundlich equation, have no upper bound on the capacity. The third requirement exists so that the capacity does not decrease as the concentration increases, a physically unrealistic situation that can occur with some polynomial isotherm functions.

The third criterion is that the isotherm function should have utility, i.e., the isotherm is usable for the various calculations that are performed. Ideally, this would mean that it is possible to analytically calculate the capacity from the concentration, and also analytically calculate the concentration from the capacity. This is not always the case. For example, the Myers isotherm (Jossens et al., 1987) gives the concentration as a function of capacity. This function cannot be analytically inverted; thus, determining the capacity for a given concentration can be accomplished only by solving for the root of an equation, a slow process computationally.

Appendix 1 shows the mathematical form and abbreviations used for the 15 isotherms studied. Table 1 shows which criteria each isotherm function meets. Only the Langmuir, BET, and Toth isotherms met all criteria. The HK, DA, and MJ isotherms met all criteria except for low concentration performance, i.e., they do not reduce to Henry's Law. All other functions did not fulfill at least two criteria.

Table 2. Physical properties of adsorbents studied.

Property	Ambersorb 563	Ambersorb 572	Filtrasorb 400
Surface area* (m²/g)	550	1100	1100
Pore volume distribution** (cm²/g)			
Micropore	0.23	0.41	0.48
Mesopore	0.14	0.19	0.09
Macropore	0.23	0.24	0.04
Water adsorbtion at 94% Relative Humidity (g/g)	0.12	0.31	0.44
Bulk density (g/cm³)	0.53	0.49	0.39
Particle size (US Sieve Series)	20–50	20–50	12–40

*BET single point surface area, micromeritics 2300.
**N$_2$ porosimetry, micromeritics 2400.

2 Procedures

A. Experimental

Three adsorbents were chosen for this study. They are Filtrasorb 400 GAC, available from the Calgon Carbon Corporation (Pittsburgh, PA), and Ambersorb 563 and 572 adsorbents, available from the Rohm and Haas Company (Philadelphia, PA). The adsorbents were used as supplied by the manufacturer. The only pretreatment was drying in an oven at 105°C for at least 4 hr before samples were weighed out.

Typical properties of these adsorbents are given in Table 2. Single point BET surface areas were obtained using a Flowsorb II 2300 surface area analyzer (Micromeritics, Norcross, GA). Pore volume distributions were obtained using an ASAP 2400 Nitrogen porosimetry analyzer (Micromeritics, Norcross, GA). Micropore volumes were determined using t-plots by the Harkins-Jura method. Mesopore volumes are the difference between the quantity of nitrogen adsorbed at a relative pressure of 0.95 and the micropore volume. Macropore volumes were determined by the quantity of nitrogen adsorbed between relative pressures of 0.95 and 0.995. Water-vapor isotherms were obtained by equilibrating the sample in a dessicator over a constant humidity sulfuric acid solution. Ambersorb 563 adsorbent has the lowest micropore volume and water vapor adsorption capacity of the three adsorbents studied. Filtrasorb 400 GAC has the highest micropore volume and water adsorption capacity, as well as the lowest meso- and macropore volume, of the adsorbents studied.

The adsorbate for this study was 1,1,2-trichloroethene, or TCE. This compound was chosen for several reasons. First, it is a very common contaminant of groundwater. TCE was found in 91 out of 945 wells tested for the Ground Water Supply Survey (Westrick et al., 1984) and in 246 out of 1035 Superfund sites evaluated in 1989 (Pasha Publications, 1989). Second, aqueous TCE concentrations can be easily analyzed over a $> 5 \times 10^5$ range using a gas chromatograph (GC). This wide concentration range is required if an accurate determination of the isotherm curvature is to be made. Many other common contaminants have either solubilities which are too low or limits of detection which are too high.

The TCE used for this study was Certified ACS Reagent Grade (Fisher Scientific, Pittsburgh, PA). According to the manufacturer, it is stabilized with 20 ppm of diisopropyl amine. Analysis of the TCE by gas chromatograph showed the presence of trace quantities of other chlorinated species, specifically chloroform, carbon tetrachloride, 1,1,1-trichloroethane, 1,1,2-trichloroethane, and 1,1,2,2-tetrachloroethene. The total concentration of these contaminants was 0.04%. The TCE was used without further purification.

The adsorption isotherms were measured using the bottle point technique (Randtke and Snoeyink, 1983). Known weights of dry adsorbent were placed in a serum
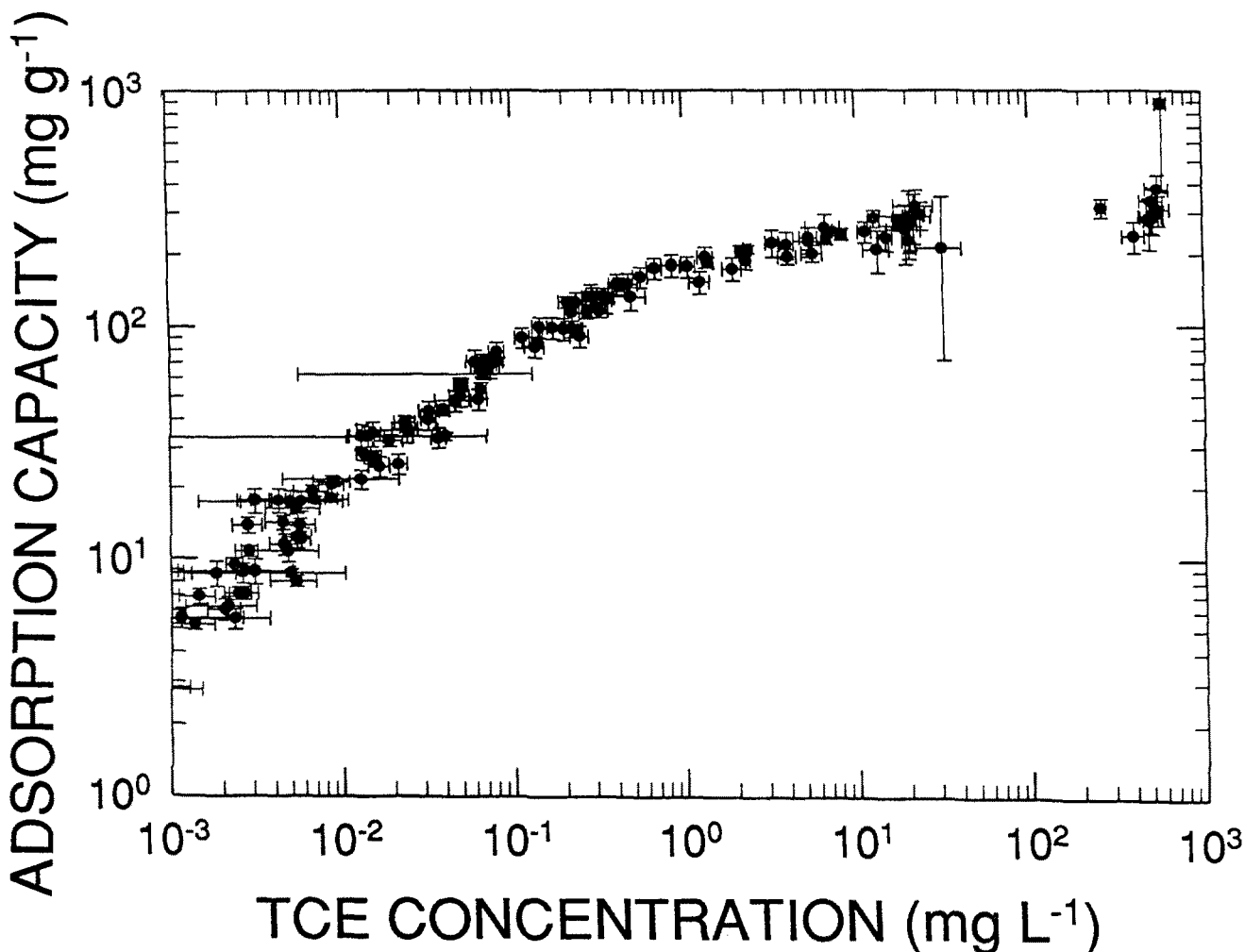
Fig. 1. Raw data for TCE adsorption isotherm on Ambersorb 563 adsorbent.

bottle filled with a known volume of TCE solution. The influent concentration was provided by four additional serum bottles containing the TCE solution without any adsorbent. Reagent water produced by a Milli-Q system (Millipore, Bedford, MA) was used for all solutions. The bottles were shaken for approximately 2 wk at room temperature. Aliquots were then removed from the serum bottles and analyzed by direct aqueous injection on a 5890A GC (Hewlett-Packard, Palo Alto, CA) equipped with a split injector, a 30 m by 0.53 mm diameter VOCOL capillary column (Supelco, Bellefonte, PA), and an electron capture detector. This system has a detection limit < 1 μg/L, and can handle sample concentrations as high as 600 mg/L without overloading the detector. Each serum bottle was analyzed in duplicate.

The adsorption capacity and uncertainty were calculated from Eq. (1) and (2),

$$q = \frac{V \times (c_i - c_f)}{m} \tag{1}$$

$$\sigma_q = q \times \sqrt{\left(\frac{\sigma_V}{V}\right)^2 + \left(\frac{\sigma_m}{m}\right)^2 + \frac{\sigma_{c_i}^2 + \sigma_{c_f}^2}{(c_i - c_f)^2}} \tag{2}$$

where q is the capacity, V is the solution volume, m is the mass of adsorbent, c_i and c_f are the initial and final concentrations, and σ is the appropriate uncertainty. Figure 1 shows the raw TCE isotherm data on Ambersorb 563 adsorbent. These data are the result of 20 separate isotherm experiments and come from three sources: there are 118 points from this laboratory, plus an additional 20 points from two university laboratories

Table 3.   Curve fit numerical results.

| Isotherm | Coef. | Ambersorb 563 | | Ambersorb 572 | | Filtrasorb 400 | | Ave. |
		χ^2/ν	Rel. Perf.	χ^2/ν	Rel. Perf.	χ^2/ν	Rel. Perf.	Rel. Perf.
Freundlich	2	18.033	15.426	16.409	6.840	6.626	4.876	9.05
Langmuir	2	5.031	4.304	13.649	5.689	16.646	12.249	7.41
BET	2	4.692	4.014	11.899	4.960	13.989	10.294	6.42
Myers	3	6.260	5.355					
RP	3	2.466	2.109	22.335	9.310	2.664	1.960	4.46
2nd Ln Poly	3	1.476	1.263	3.355	1.398	1.604	1.180	1.28
DA	3	1.324	1.133	3.366	1.403	1.452	1.068	1.20
Toth	3	1.265	1.082	3.862	1.610	1.644	1.210	1.30
HK	3	1.175	1.005	2.716	1.132	1.359	1.000	1.05
MJ	4	1.169	1.000	2.399	1.000	1.419	1.044	1.01
EI-1	2	18.033	15.426	16.409	6.840	6.626	4.876	9.05
EI-2	3	1.476	1.263	3.355	1.398	1.604	1.180	1.28
EI-3	4	1.320	1.129	2.458	1.025	1.434	1.055	1.07
EI-4	5	1.188	1.016	2.629	1.096	1.387	1.021	1.04
EI-5	6	1.173	1.003	2.857	1.191	1.443	1.062	1.09

under contract to Rohm and Haas Company. There is excellent agreement among the three sources.

The other adsorbents have not been studied in as much detail. For Ambersorb 572 adsorbent, there are 14 points from our laboratory and 3 from a university laboratory, for a total of 17 points. For Filtrasorb 400 GAC, there are 22 points from our laboratory and 4 from a university laboratory, for a total of 26 points. There is also excellent agreement between the sources for these adsorbents.

B. Data Reduction

Weighted nonlinear least-squares regression was used to determine the optimum coefficients for each isotherm function. Because of an unusual characteristic of the isotherm data, it was necessary to carry out the curve fitting in two steps. First, there was a preliminary curve fit in order to calculate the appropriate weighting factors. Second, there was a final curve fit to all of the equations using these weighting factors.

A standard assumption in least-squares regression is that all of the uncertainty is on the dependent variable, with no uncertainty for the independent variable (Bevington, 1969b). For most of the equations evaluated, the dependent variable is adsorption capacity while the independent variable is the equilibrium concentration. Isotherm data are unusual in the sense that the uncertainty in the concentration is typically larger

than the uncertainty in the capacity, especially at low concentrations. Under these unusual circumstances, an adjusted uncertainty is required. This adjusted uncertainty is obtained from the uncertainties in both concentration and capacity by Eq. (3):

$$\sigma_{\rm adj} = \sqrt{\sigma_{\rm Capacity}^2 + {\rm Slope}^2 \times \sigma_{\rm Concentration}^2} \qquad (3)$$

where "Slope" is the slope of the isotherm and σ is the appropriate standard deviation. This adjusted uncertainty is then used to determine the weighting factors. Since the weighting factors depend on the results from the curve fit, and the results of the curve fit depend on the weighting factors, an iterative procedure is necessary.

This iterative procedure is very slow. Additionally, each isotherm function has a slightly different set of weighting factors, making it difficult to compare different isotherm functions. Thus, one functional form, the DA equation, was used to obtain "typical" weighting factors. All subsequent curve fits were performed using these "typical" weighting factors.

3   Results

A.   Numerical Results

The numerical results from the curve fits are shown in Table 3. The χ^2/ν statistic from all curve fits are given.

To better compare the relative performance of each function, the relative performance number compares the χ^2/ν for each function against the best function for that adsorbent. The lower the number, the better the function performed relative to the other functions.

The lowest χ^2/ν's obtained for Ambersorb 563 and 572 adsorbents and Filtrasorb 400 GAC were 1.169, 2.399, and 1.359, respectively. These values are all greater than the expected value of 1; thus, either none of the isotherm functions evaluated are accurate representations of the actual isotherm function, or the scatter in the data is slightly larger than the experimental uncertainties. Visually, the best fits do an excellent job of representing the data. Thus, it is believed that the larger than expected values of χ^2/ν are the result of scatter in the data exceeding the experimental uncertainties.

It is possible to estimate the ratio of the actual experimental uncertainties to the expected experimental uncertainties by taking the square root of χ^2/ν (Bevington, 1969a). This ratio is 1.08, 1.55. and 1.17 for Ambersorb 563 and 572 adsorbents and Filtrasorb 400 GAC, respectively. Thus, for Ambersorb 563 adsorbent, the average experimental error was 8% greater than the experimental error originally assigned to each point. Considering that the Ambersorb 563 data came from 20 experiments over 3 years by 3 different laboratories, this excess scatter is not considered to be very significant. An examination of Fig. 1 shows very little scatter for concentrations greater than roughly 0.01 mg/L and less than 100 mg/L. Only for low concentrations near the detection limit or at high concentrations does the scatter become large. Similar conclusions are drawn for the other two adsorbents.

B. Optimum Curve Fit

Examination of Table 3 shows that the best overall curve fit was the Marczewski and Jaroniec (MJ) isotherm, which requires four coefficients. The second best overall curve fit was the 4th order exponential isotherm equation (EI-4), which has five coefficients. The best curve fits using three coefficients were the Höll-Kirch (HK) and Dubinin-Astakov (DA) equations.

Figure 2 shows these four equations for Ambersorb 563 adsorbent over a concentration range which exceeds the observations by an order of magnitude at each end. For concentrations between 0.002 and 500 mg/L, there is essentially no difference between the

curve fits. There are slight differences when the equations are extrapolated. The DA and EI-4 equations are limited to concentrations below the solubility limit, while the HK and MJ equations are not. The DA, HK, and MJ equations all predict capacity plateaus, while the EI-4 equation predicts a slight upwards trend near the solubility limit. The major difference occurs when the equations are extrapolated to very low concentrations. The DA equation predicts the lowest capacity, the EI-4 equation predicts the highest capacity, and the HK and MJ equations predict an intermediate capacity. None of these equations extrapolate to Henry's law at low concentration. Thus, these four equations provide nearly identical representations of the data over the concentration range for which there is data, with little or no theoretical advantage for one equation over another.

However, examination of the coefficients for the various curve fits suggest that some equations have numerical advantages over the other equations. For example, the η coefficient for the MJ equation for Ambersorb 572 adsorbent has a value of 1.25 ± 0.61. At the 95% confidence level this coefficient does not differ from 0. In addition, theoretical considerations suggest that η is restricted to the range 0 to 1, a restriction that was not met in this case. Consequently, this equation is inappropriate for summarizing the results for all three adsorbents.

The second best overall curve fit was given by the EI-4 equation. However, there are also numerical problems with this equation. At the 95% confidence level, four out of five coefficients are indistinguishable from 0 for both Ambersorb 572 adsorbent and Filtrasorb 400 GAC. Thus, this equation is also inappropriate for summarizing the results for all three adsorbents.

The isotherm data was smooth and showed little curvature over a concentration range of 5 to 6 orders of magnitude; thus, only a few coefficients are required to accurately represent the experimental results. Beyond a minimum number of coefficients, additional coefficients marginally improve the quality of the curve fit at the expense of larger uncertainties in each coefficient. The numerical difficulties with the MJ and EI-4 equation are the result of these equations having more coefficients than are required to fit the data over the concentration range studied.

The third and fourth best equations were the HK and DA. There were no numerical problems for either equation with any of the adsorbents studied. Therefore, both equations are appropriate for summarizing the results for all three adsorbents.
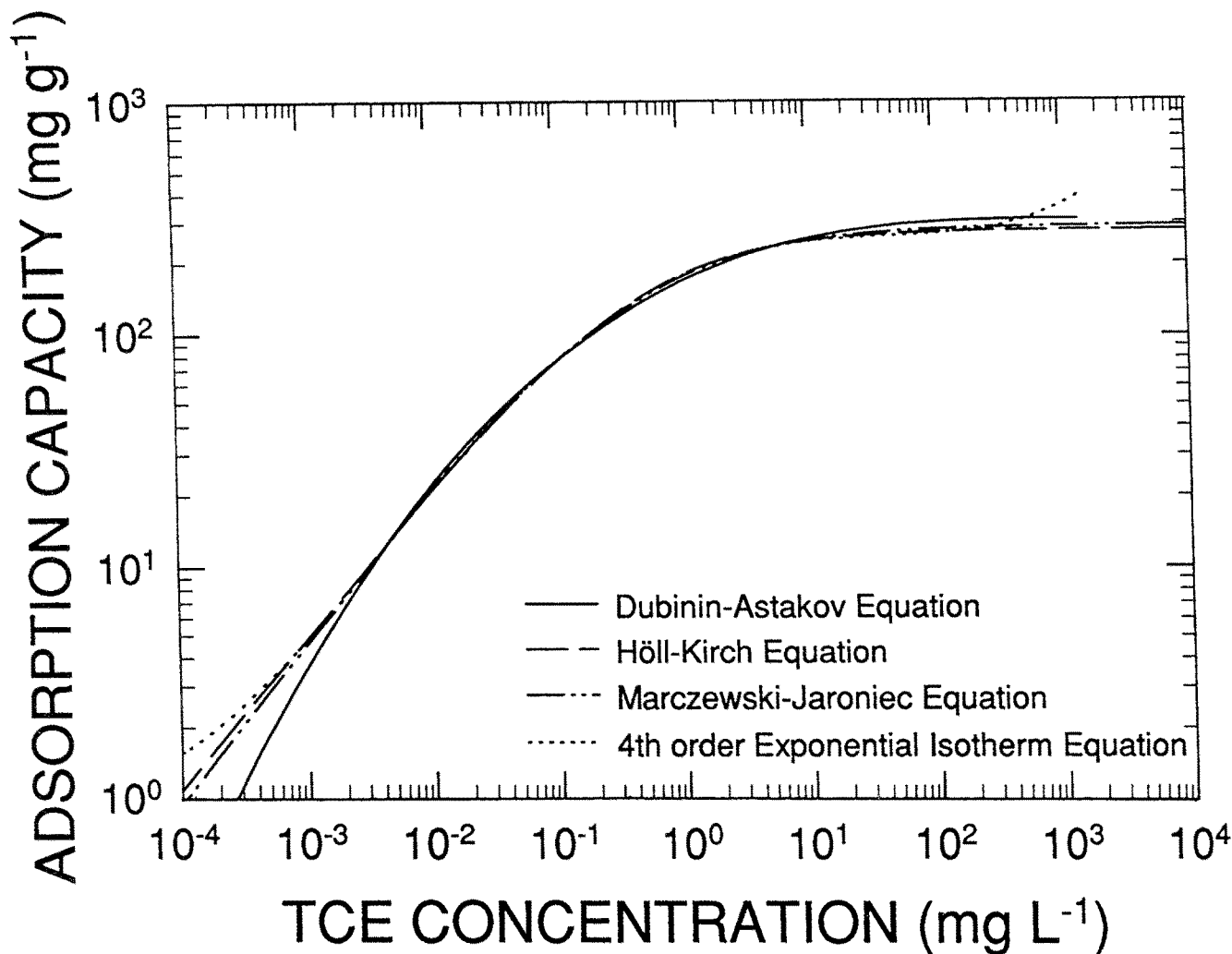
Fig. 2. Comparison of DA, HK, MJ, and EI-4 isotherm equation curve fit results for Ambersorb 563 adsorbent.

Both of these equations use only 3 coefficients. One coefficient gives the maximum capacity, while the other 2 coefficients describe the shape of the isotherm. Both equations predict comparable maximum capacities. The major difference between these isotherms is the behavior at low concentrations. Neither isotherm reduces to Henry's law at low concentrations: the HK isotherm reduces to the Freundlich isotherm, whereas the DA isotherm does not. Thus, on logarithmic axes the HK isotherm reduces to a straight line whereas the DA isotherm continues to curve downward as the concentration decreases. One of the consequences of this difference in limiting behavior is that the HK isotherm will predict higher capacities than the DA isotherm when extrapolated to low concentrations.

A second difference between the two isotherms is in the underlying physical model of adsorption. The HK isotherm is derived from a model of monolayer adsorption using the Langmuir adsorption isotherm and a surface with a heterogeneous distribution of adsorption energies. The DA isotherm is based on Dubinin's theory of micropore volume filling. As shown by Bering et al. (1972), the thermodynamics of the two models are not equivalent. Adsorption into micropores is normally assumed to take place by micropore filling. Thus, the DA isotherm makes more sense conceptually.

A third difference is that the DA isotherm has been more extensively studied. Thus, there are theories for predicting how the coefficients change for different solutes and adsorbents. For example, a general
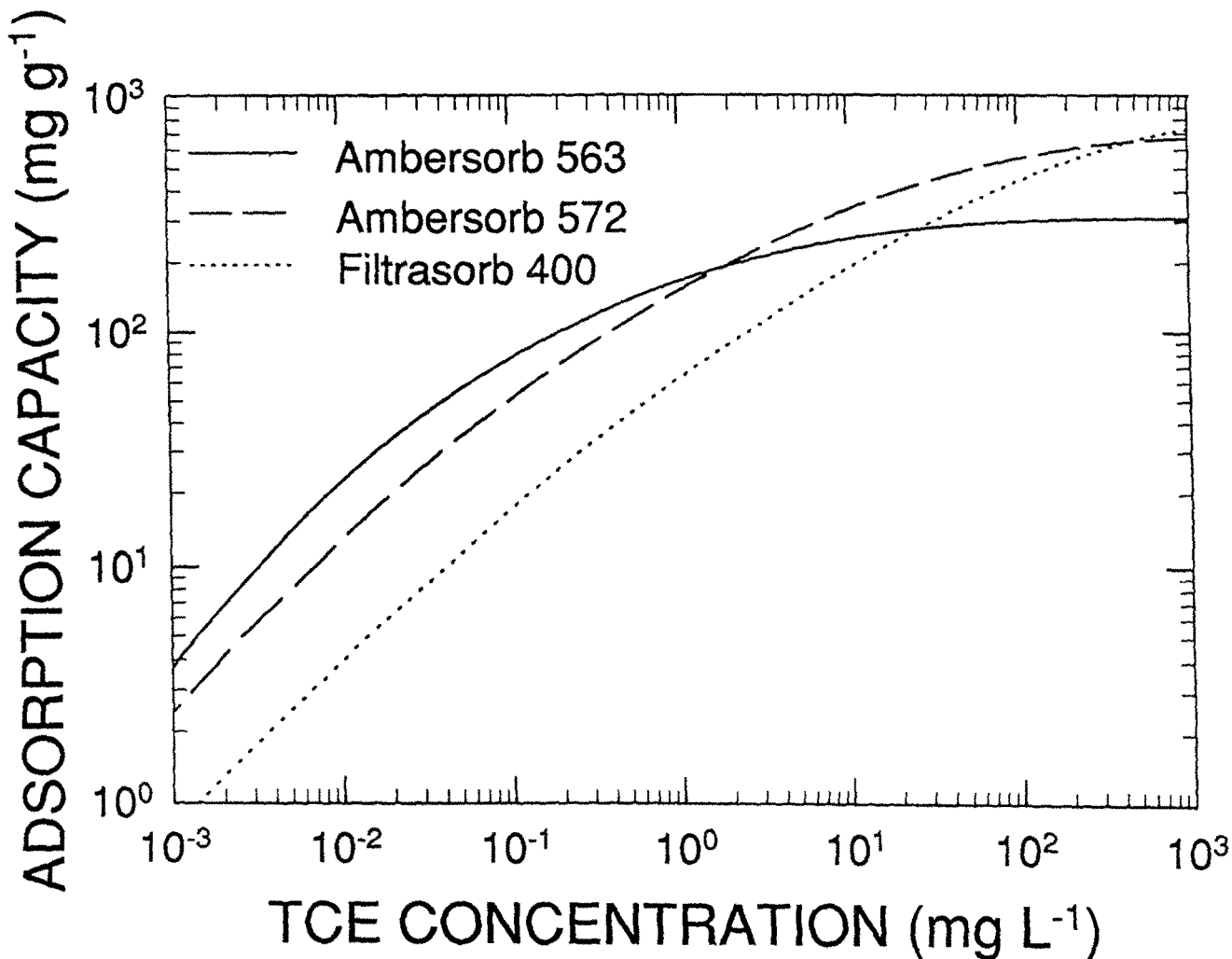
Fig. 3. DA isotherm equation curve fitting results for TCE adsorption on Ambersorb 563 and 572 adsorbents and Filtrasorb 400 GAC.

correlation based on DA type isotherms for the adsorption of organic solvents from aqueous solutions onto GAC has been determined (Speth, 1986). In addition, two general correlations based on DA type isotherms for the adsorption of vapors onto GAC were recently published (Wood, 1992, Nirmalakhandan and Speece 1993).

An examination of Table 1 shows that there is no difference between the HK and DA isotherm equations in meeting the suitability criteria. Neither equation reduces to Henry's law at low concentration, but all other criteria were met.

It was concluded that the DA isotherm is the optimum isotherm equation. There is a slight reduction in the quality of the fit compared to the best equations.

However, the improved numerical stability of the results, the conceptual framework, and the models for estimating the coefficients are all considered major advantages. In addition, the DA isotherm provides the more conservative estimate when extrapolated to low concentrations.

Figure 3 shows the DA isotherm for all three adsorbents. The capacity advantage of Ambersorb 563 adsorbents over Filtrasorb 400 GAC at low concentrations is evident. However, the isotherm for Ambersorb 563 adsorbent is more sharply curved; thus, at high concentrations Filtrasorb 400 GAC has the capacity advantage. The performance of Ambersorb 572 adsorbent is generally intermediate to the other two adsorbents.

Table 4.   Comparison to literature isotherms for F-400 GAC.

Source	Conc. range (mg/L)	TCE Capacity (mg/g) @			
		0.001 mg/L	0.010 mg/L	0.100 mg/L	1.00 mg/L
This Work	0.030–576	0.8	4.0	17.3	63.2
Browne and Cohen	0.001–1.15	2.2	6.5	19.2	56.5
Speth and Miltner	0.008–0.442	2.0	6.1	18.4	55.9
Weber et al.	0.008–0.800	1.9	6.5	22.0	73.9
Urano et al.	0.009–0.800	0.7	2.5	9.8	37.8
Benz et al.	0.009–0.900	3.3	9.4	26.9	77.4
Geometric Mean		1.8	5.7	18.3	58.5

4 Discussion

A. Comparison with Literature Values

The TCE adsorption isotherm for Filtrasorb 400 GAC has recently been measured (Browne and Cohen, 1990; Speth and Miltner, 1990; Weber et al., 1991; Urano et al., 1991; Benz et al., 1991). Table 4 compares these literature Freundlich isotherm capacities with the results from this work.

The TCE isotherm from this work is within 10% of the literature values at higher concentrations. The deviation increases when extrapolating to lower concentrations, reaching 30% at 0.01 mg/L. This increase in deviation at low concentrations is not unexpected since the DA isotherm has more curvature than the Freundlich isotherm. However, at all concentrations from 0.001 to 1 mg/L the results from this work are within the scatter of the published isotherms. This agreement with the literature tends to confirm the accuracy of this work.

B. Interpretation of Coefficients

The DA isotherm equation is

$$q = q_\infty \times \exp\left\{ - \left(\frac{A}{E}\right)^\eta \right\} \qquad (4)$$

where the adsorption potential, A, is given by

$$A = R \times T \times \ln(c_s/c) \qquad (5)$$

Each coefficient has a physical interpretation: the maximum capacity, q_∞, is related to the micropore volume;

the characteristic energy, E, is the adsorption potential at which the capacity is 36.8% of the maximum capacity and is related to the size of the micropores; and the exponent, η, gives the curvature of the isotherm and is related to the heterogeneity of the micropores. Table 5 shows the value of these coefficients for each adsorbent.

1. Micropore Volume. The limiting capacity of the DA isotherm is reached when the micropores are completely filled. Thus, it is possible to estimate the micropore volume by assuming a density for the adsorbed material. Pure TCE has a density of 1.460 g/cm^3 at 25°C (Riddick et al., 1986). Table 6 shows the estimated micropore volumes from the DA isotherm and compares them with the values obtained by N_2 porosimetry using a ASAP 2400 N_2 porosimeter (Micromeritics, Norcross, GA). Micropore volumes were obtained using t-plots by the Harkins Jura method.

It has been shown that in some instances the micropore volumes obtained from the DR isotherm (DA isotherm with $\eta = 2$) can be erroneous (Sircar, 1987). However, for this work there is excellent agreement between the TCE micropore volumes and the N_2 micropore volumes. The disagreement for Ambersorb 563 was 9 ± 6%, which is not a statistically significant result. For the other two adsorbents, the disagreement was less than the experimental error. Thus, the two independent methods of estimating micropore volume, t-plot analysis of N_2 isotherm and DA analysis of aqueous TCE isotherm, give the same micropore volume to within experimental error.

Therefore, the plateau observed in the TCE adsorption isotherm is the result of micropore filling. Thus,

Table 5.   DA isotherm coefficients for TCE adsorption.

Adsorbent	Maximum capacity (mg/g)	Characteristic energy (kJ/mol)	Exponent
Ambersorb 563	308.7 ± 9.1	21.08 ± 0.25	2.93 ± 0.08
Ambersorb 572	672.7 ± 72.6	14.62 ± 0.89	1.98 ± 0.17
Filtrasorb 400	746.8 ± 60.6	9.89 ± 0.50	1.52 ± 0.07

Table 6.   Adsorbent micropore volumes.

Adsorbent	Maximum capacity (mg/g)	Estimated micropore volume (cm³/g)	N₂ micropore volume (cm³/g)	Ratio (%)
Ambersorb 563	308.7 ± 9.1	0.21 ± 0.01	0.23 ± 0.01	91 ± 6
Ambersorb 572	672.7 ± 72.6	0.46 ± 0.05	0.41 ± 0.02	112 ± 13
Filtrasorb 400	746.8 ± 60.6	0.51 ± 0.04	0.48 ± 0.02	106 ± 9

the higher capacity at high concentrations for Filtrasorb 400 GAC is the result of its higher micropore volume.

2.   Thermodynamic Interpretation.   Several thermodynamic properties of adsorption can be extracted from the adsorption isotherm. These include the adsorption potential distribution as well as the enthalpy and entropy of adsorption. Using the condensation approximation, the following equations are obtained when solved for the DA isotherm equation (Jaroniec et al., 1988),

$$\theta = \frac{q}{q_\infty} = \exp\left\{-\left(\frac{A}{E}\right)^\eta\right\} \qquad (6)$$

$$X(A) = \frac{\eta}{E} \times \left(\frac{A}{E}\right)^{\eta-1} \times \exp\left\{-\left(\frac{A}{E}\right)^\eta\right\} \qquad (7)$$

$$\Delta H = A - \frac{\alpha_e \times T \times E}{\eta} \times \left(\frac{E}{A}\right)^{\eta-1} \qquad (8)$$

$$\Delta S = -\frac{\alpha_e \times E}{\eta} \times \left(\frac{E}{A}\right)^{\eta-1} \qquad (9)$$

where θ is the relative adsorption or fraction of micropores filled, $X(A)$ is the adsorption potential distribution, ΔH and ΔS are the differential molar enthalpy and entropy of adsorption, and α_e is the thermal coefficient for the maximum capacity.

The thermal coefficient for the maximum capacity, α_e, has not been measured experimentally. To do

so would require measuring the isotherm at multiple temperatures. As a first approximation, one can use the coefficient of thermal expansion of TCE, $\alpha_e = 1.15 \times 10^{-3}$, for the calculations.

Figures 4–7 show the four thermodynamic quantities evaluated for all three adsorbents using the DA isotherm. In these figures the thermodynamic quantity is plotted as a function of adsorption potential or TCE concentration at 25°C. It should be remembered that these results were calculated assuming the DA adsorption isotherm. This model is appropriate for adsorption in micropores. However, adsorption in mesopores and macropores has not been considered. Thus, the shape of the curves for high concentrations, or low adsorption potentials, might be different than shown here. However, since most adsorption of interest is at low concentrations within micropores, ignoring the effects of mesopores and macropores should not affect the conclusions drawn.

The adsorption energy distribution, Fig. 5, is the key result describing the thermodynamics of adsorption. This distribution provides information as to the strength and heterogeneity of the adsorbate-adsorbent interactions. All other thermodynamic quantities can be calculated from this distribution. In addition, this distribution is nearly invariant with temperature. Thus, knowledge of the adsorption potential distribution at one temperature allows one to calculate thermodynamic quantities at other temperatures.
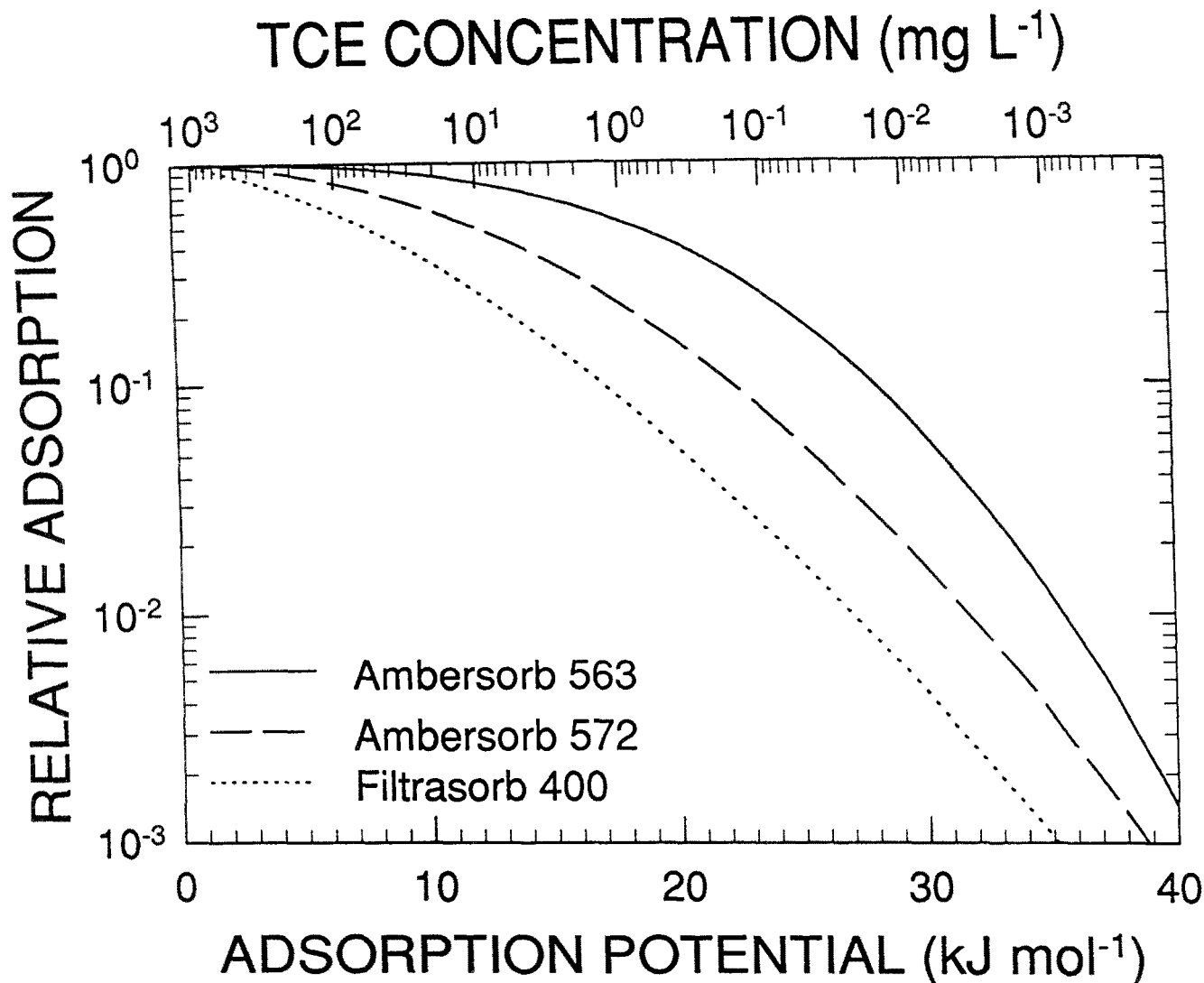
TCE CONCENTRATION (mg L⁻¹)

Fig. 4. Relative adsorption as a function of adsorption potential and TCE concentration derived from DA isotherm results.

One of the advantages of the DA isotherm is that many quantities related to the adsorption energy distribution are easily calculated. For example, the mode, or peak of the distribution, is

$$A_{\text{Mode}} = E \times \left(1 - \frac{1}{\eta}\right)^{\frac{1}{\eta}} \qquad (7)$$

the mean of the distribution is

$$\langle A \rangle = E \times \Gamma\left(1 + \frac{1}{\eta}\right) \qquad (8)$$

the standard deviation of the distribution is

$$\sigma_A = E \times \sqrt{\Gamma\left(1 + \frac{2}{\eta}\right) - \Gamma^2\left(1 + \frac{1}{\eta}\right)} \qquad (9)$$

and the coefficient of variation of the distribution is

$$\text{COV} = \frac{\sigma_A}{\langle A \rangle} = \frac{\sqrt{\Gamma\left(1 + \frac{2}{\eta}\right) - \Gamma^2\left(1 + \frac{1}{\eta}\right)}}{\Gamma\left(1 + \frac{1}{\eta}\right)} \qquad (10)$$

where $\Gamma(x)$ is the gamma function. Table 7 summarizes these key quantities describing the adsorption potential distribution for the three adsorbents.
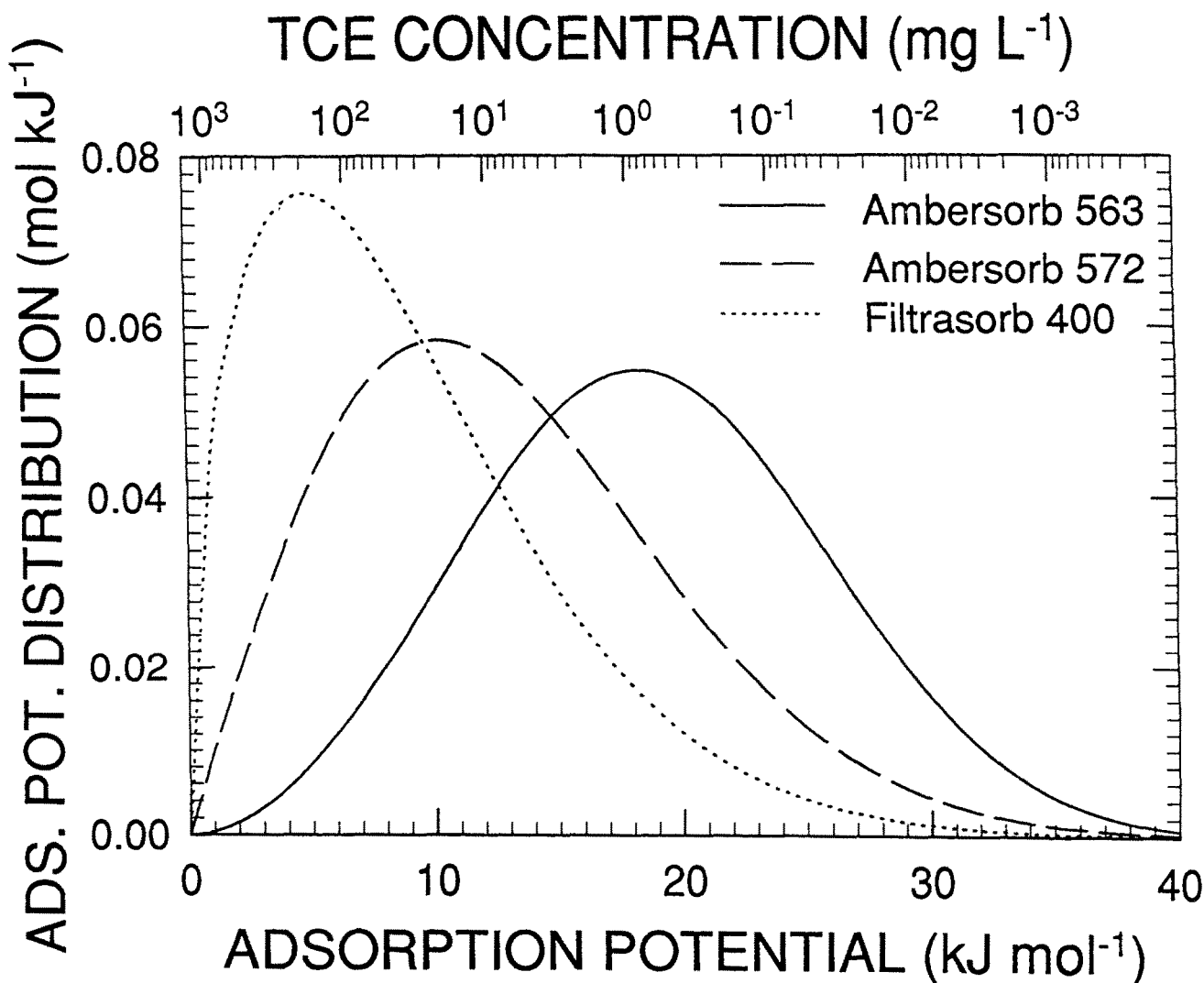
Fig. 5.   Adsorption potential distribution as a function of adsorption potential and TCE concentration derived from DA isotherm results.

As is evident from both Fig. 5 and Table 7, there are significant differences in the adsorption energy distribution for the three adsorbents. The distribution for Ambersorb 563 adsorbent is nearly symmetrical, whereas that for Filtrasorb 400 GAC is extremely skewed. The mean for Ambersorb 563 adsorbent is 18.8 kJ/mol, which is slightly more than twice the mean for Filtrasorb 400 GAC. All three adsorbents have standard deviations between 6 and 7 kJ/mol. The coefficient of variation for Ambersorb 563 adsorbent is 0.37, which is slightly less than one-half of that for Filtrasorb 400 GAC. Ambersorb 572 adsorbent is intermediate to the other two adsorbents.

Therefore, Ambersorb 563 adsorbent has the highest energy, most homogeneous adsorption volume of the 3 adsorbents studied, while Filtrasorb 400 GAC has the lowest energy, least homogeneous adsorption volume.

The position of the adsorption potential distribution is given primarily by the characteristic energy, E. For vapor phase adsorption, the characteristic energy is related to the size of the micropores (Bansal et al., 1988). An inverse relationship was found between the characteristic energy from benzene vapor adsorption and the gyration radius of the micropores from small angle X-ray scattering for a series of carbons. Vapor
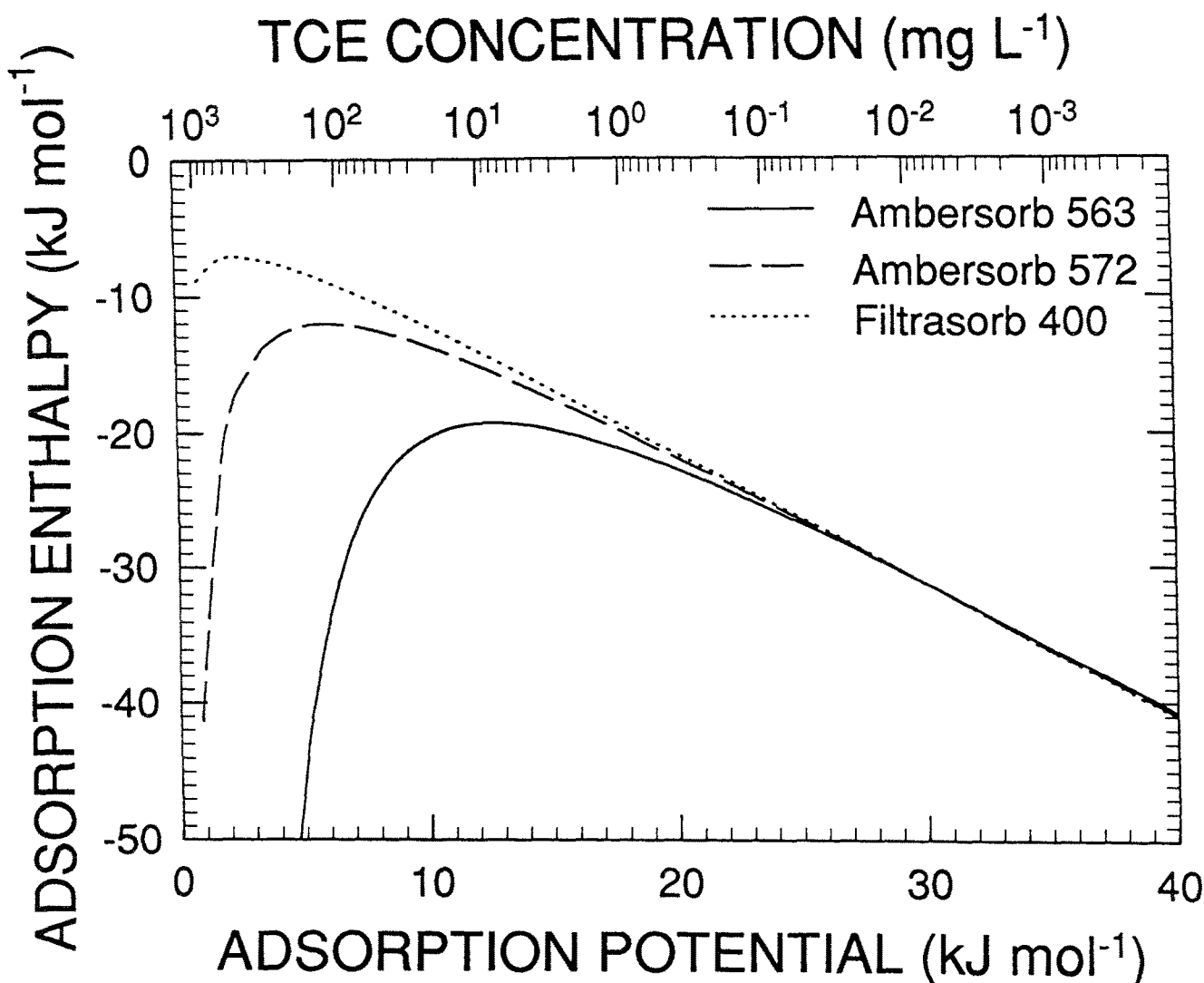
Fig. 6.   Adsorption enthalpy as a function of adsorption potential and TCE concentration derived from DA isotherm results.

phase adsorption involves adsorbate-adsorbent interactions, whereas aqueous phase adsorption also involves adsorbate-solvent and solvent-adsorbent interactions. As shown in Table 2, Ambersorb 563 adsorbent is significantly more hydrophobic than either of the other two adsorbents studied. However, it has not been determined how much of the differences in characteristic energy is the result of differences in pore size distribution and how much is the result of differences in water-adsorbent surface interactions. Therefore, it is not known if an inverse relationship similar to that for vapor phase adsorption would hold for aqueous phase adsorption.

The heterogeneity of the adsorption potential distribution is primarily a function of the exponent, η (Bansal et al., 1988). The absolute heterogeneity is given by the standard deviation. The shape, or curvature, of the isotherm is a function of the heterogeneity relative to the mean. Thus, the shape of the isotherm is a function of the coefficient of variation, which is a function only of η. Heterogeneous micropores lead to relatively wide adsorption potential distribution, which lead to very little curvature in the overall adsorption isotherm. Conversely, homogeneous micropores lead to a relatively narrow adsorption potential distribution, which lead to large curvature in the overall adsorption isotherm
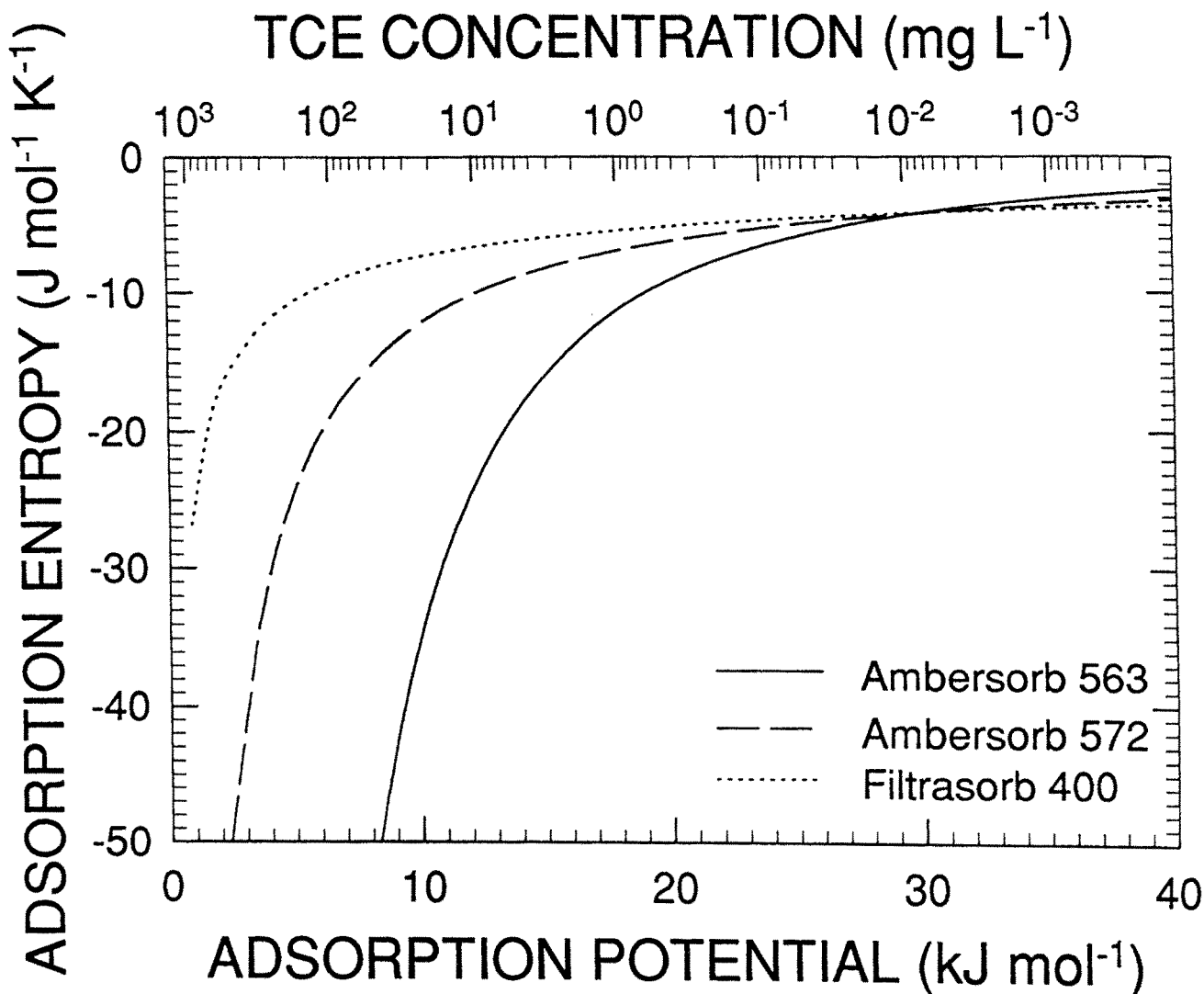
Fig. 7. Adsorption entropy as a function of adsorption potential and TCE concentration derived from DA isotherm results.

when plotted on logarithmic axes. For vapor phase GACs, η varies practically from 1.5 to 3. Strongly activated and heterogeneous carbons have values of η as low as 1.5, while values of η as high as 3.0 are associated with relatively homogeneous micropores. Ambersorb 563 adsorbent has an η of 2.93, indicative of relatively homogeneous micropores. Filtrasorb 400 GAC has an η of 1.52, indicative of heterogeneous micropores. Ambersorb 572 adsorbent has an η of 1.98, which is intermediate to the other two adsorbents. Thus, the large curvature of the Ambersorb 563 adsorbent isotherm is the result of relatively homogeneous micropores.

Figures 6 and 7 show the calculated differential molar enthalpy and entropy of adsorption as a function of adsorption potential or TCE concentration. At low concentrations there is little difference between the three adsorbents. The differences become very large for concentrations greater than roughly 1 mg/L.

It is common to plot the differential molar enthalpy and entropy of adsorption as a function of relative adsorption, or the fraction of micropores filled, as seen in Figs. 8 and 9. There is almost no difference between the three adsorbents with respect to the differential entropy of adsorption. The differential

Table 7. Key properties of TCE adsorption potential distribution.

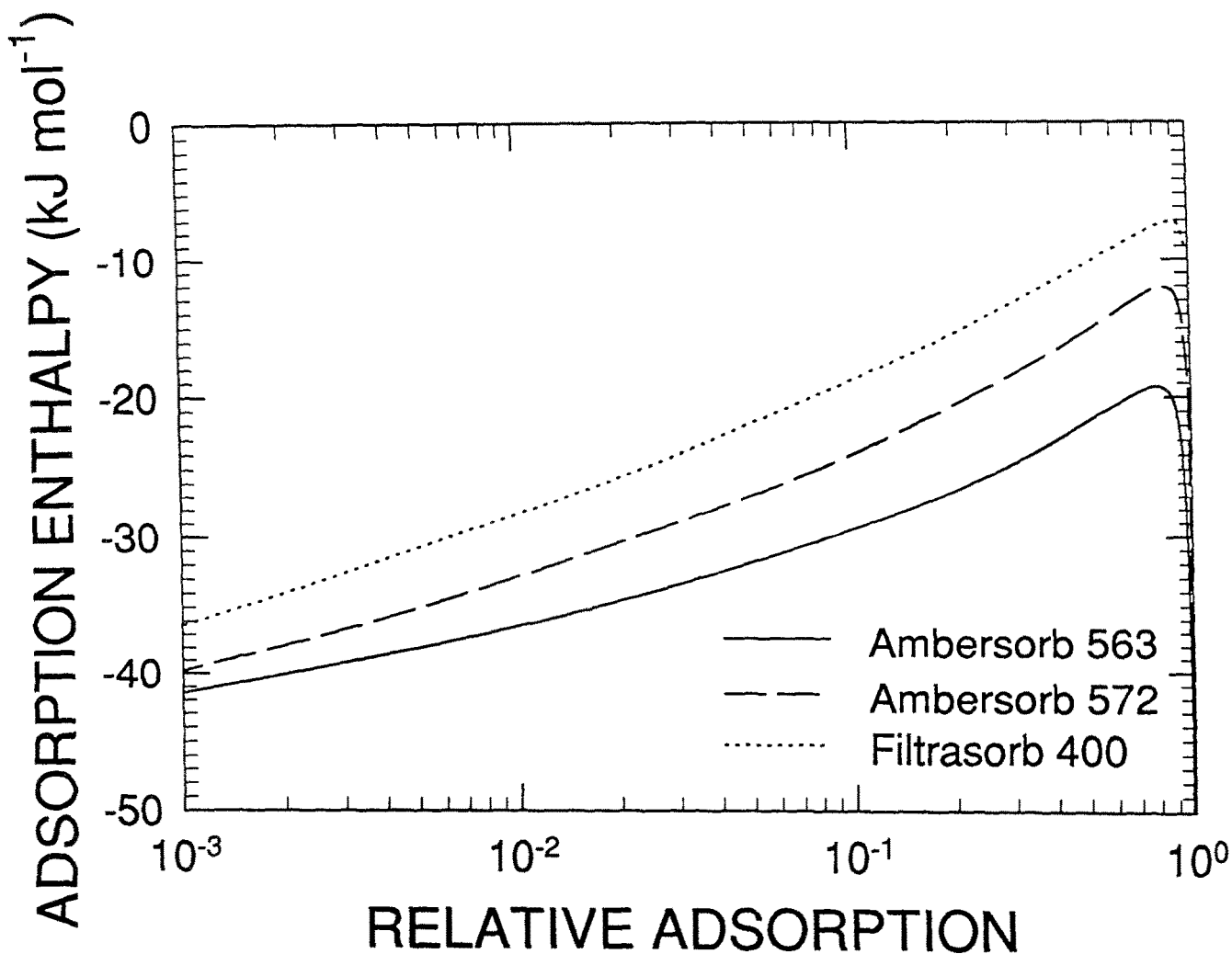| Adsorbent	Mode (kJ/mol)	Mean (kJ/mol)	Standard deviation (kJ/mol)	Coefficient of variation
Ambersorb 563	18.28	18.81	6.98	0.371
Ambersorb 572	10.25	12.96	6.84	0.527
Filtrasorb 400	4.88	8.91	5.98	0.671

Fig. 8. Adsorption enthalpy as a function of relative adsorption, derived from DA isotherm results.

enthalpies of adsorption for the three adsorbents are nearly parallel curves, with Ambersorb 563 adsorbent roughly 8 kJ/mol more exothermic than Filtrasorb 400 GAC.

C. Validity of DA Equation

The DA isotherm does have some limitations. Most significantly, it does not reduce to Henry's law at low
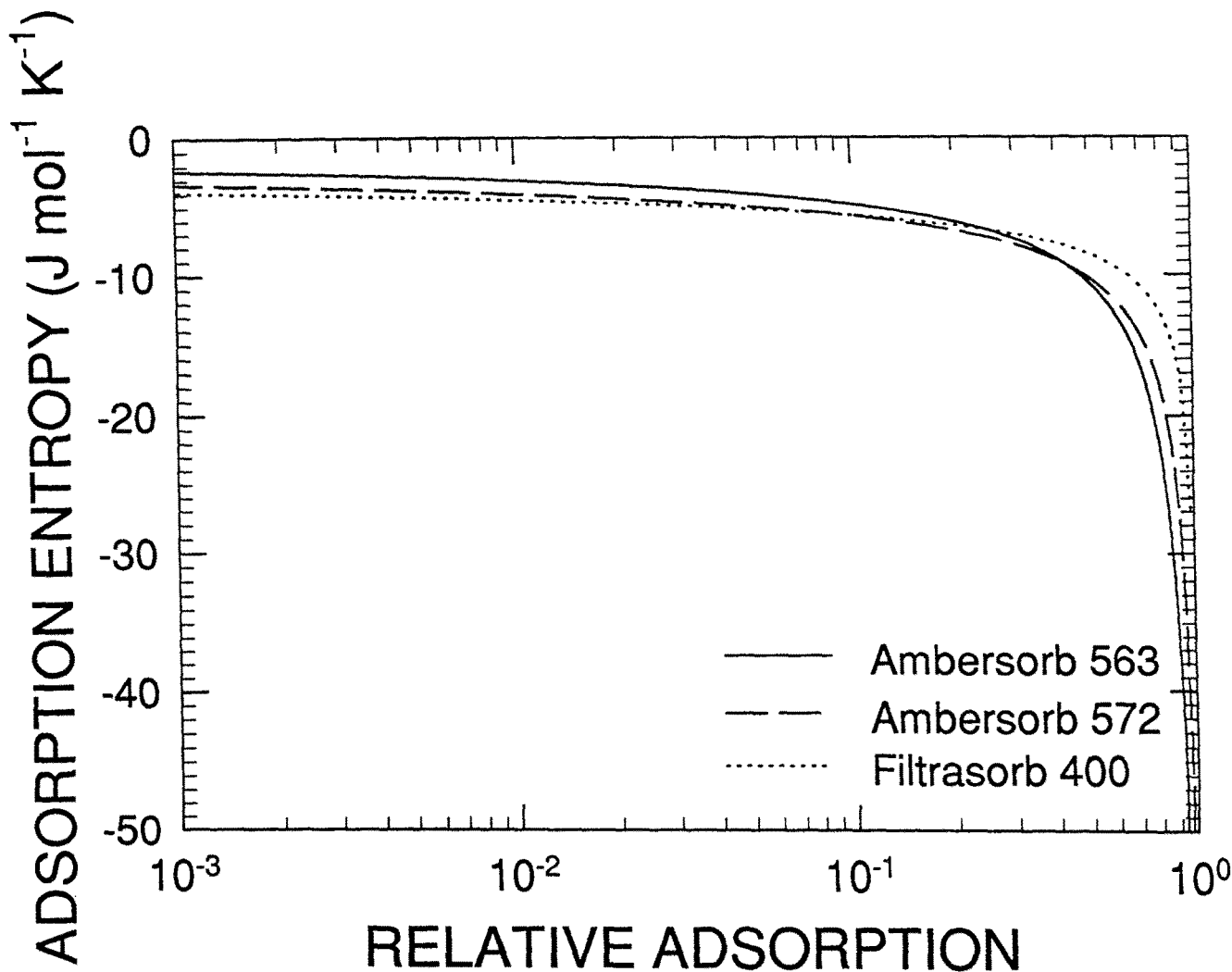
Fig. 9.   Adsorption entropy as a function of relative adsorption, derived from DA isotherm results.

concentrations. This can lead to thermodynamic inconsistencies. However, the Henry's law regime was not reached in the concentration range covered by this work, a range of 6 orders of magnitude. If data is obtained at lower concentrations where Henry's law is applicable, then another isotherm equation would be required.

The DA isotherm assumes a microporous adsorbent. It cannot predict the adsorption into meso- and macropores which will occur at very high concentrations. Conversely, if data is obtained at these high concentrations, then the DA isotherm can give incorrect micropore volumes. For the adsorbents covered in this work, the micropore volumes obtained by the DA analysis of the TCE isotherm agreed with those

obtained from N_2 porosimetry. If data is obtained at higher concentrations where meso-and macropore adsorption occurs, then another isotherm equation would be required.

Several predictions can be made from the DA isotherm equation. First, the characteristic energy and the exponent should be independent of temperature. Thus, the current DA isotherm coefficients can be used to predict the TCE isotherm at temperatures other than 25°C. Such a prediction would require knowing the density and solubility of TCE as a function of temperature. The comparison of predicted to an experimental isotherm would be a sensitive test of the validity of the DA isotherm equation to these adsorbents.

Second, models have been developed for the DA and DR equation which predict how the characteristic energy changes for different solutes. These include an aqueous phase adsorption correlation (Speth, 1986) as well as vapor phase adsorption correlations (Wood, 1992; Nirmalakhandan and Speece, 1993). The maximum capacity is generally the product of the micropore volume and the adsorbate density. The characteristic energy is generally a function of the molar volume of the adsorbate or a related parameter (polarizability, molar refractivity, parachor, first-order connectivity index, etc.) The exponent is considered constant. If these correlations are found to apply, this provides another sensitive test of the validity of the DA isotherm equation to these adsorbents.

5   Conclusions

Aqueous adsorption isotherms for GAC and other adsorbents are generally interpreted using the Freundlich isotherm equation. This work has shown that the DA isotherm equation provides a significantly better representation of the experimental data for Filtrasorb 400 GAC and Ambersorb 563 and 572 carbonaceous adsorbents. The DA isotherm can be used over a much wider range of concentrations than the Freundlich isotherm.

Ambersorb 563 adsorbent has 5 to 10 times the capacity of Filtrasorb 400 GAC for small chlorinated molecules at low concentrations, in spite of having less than 50% of the micropore volume. This work provides a thermodynamic basis for understanding the differences between these adsorbents. Ambersorb 563 adsorbent has a significantly more energetic, more homogeneous adsorption volume than Filtrasorb 400 GAC.

There are limitations to the DA equation. However, these limitations were not apparent in this work. It is possible to predict the isotherm at other temperatures and for other adsorbates given the current DA isotherm coefficients and several theories and correlations. A sensitive test of the model would be to verify these predictions experimentally.

6   Appendix I: List of Isotherm Equations

There are numerous isotherm equations which have been developed over the years to describe vapor-phase and liquid-phase adsorption. This appendix shows the equations that were used for this study. All equations can be found in the following sources (Sontheimer et

al., 1985a; Derylo Marczewska and Jaroniec, 1987; Jaroniec and Madey, 1988). The nomenclature of the various sources was modified to be consistent and to make it easier to determine the major role of the various adjustable parameters.

A.   Two Coefficient Isotherm Equations

1.   Freundlich Isotherm. Freundlich proposed in 1906 a simple power function isotherm equation. This equation is commonly used for representing aqueous-phase adsorption onto GACs and comparable adsorbents. The Freundlich equation is given by

$$q = K \times c^{\eta}. \qquad (I.1)$$

At low concentration, the Freundlich equation does not reduce to Henry's law, and at high concentrations it predicts an infinite capacity. However, empirically this equation does a very good job of representing aqueous-phase adsorption onto GACs and comparable adsorbents. This isotherm is used in a recent compilation of GAC adsorption isotherms (Speth and Miltner, 1990).

2.   Langmuir Isotherm. The Langmuir isotherm was developed in 1918 for the adsorption of gases on solid surfaces. It can be derived by either simple kinetic considerations or from statistical thermodynamics. The Langmuir equation describes the adsorption of a monolayer onto a homogeneous surface. When modified for aqueous-phase adsorption, the Langmuir isotherm equation is given by

$$q = q_m \times \frac{K \times c}{1 + K \times c}. \qquad (I.2)$$

At low concentrations, the Langmuir equation reduces to Henry's law. At high concentrations, the capacity approaches a maximum value, q_m, the monolayer capacity.

3.   BET Isotherm. The Brunauer-Emmett-Teller (BET) equation is often used to describe the adsorption of a gas on a solid surface. This model incorporates multilayer formation onto a homogeneous surface. When modified for aqueous-phase adsorption, the BET equation is given by

$$q = q_m \times \frac{K \times \frac{c}{c_s}}{\left(1 - \frac{c}{c_s}\right) \times \left(1 - \frac{c}{c_s} - K \times \frac{c}{c_s}\right)}. \qquad (I.3)$$

This equation reduces to Henry's Law at low concentration. At intermediate concentrations, there can be a plateau at the monolayer capacity, followed by additional capacity at higher concentrations due to multilayer formation.

B.   Three Parameter Isotherm Equations

1.   Myers Isotherm.

The Myers equation (Jossens et al., 1978) is given by

$$c = \frac{q}{K} \times \exp\{\alpha \times q^{\eta}\}. \tag{I.4}$$

The Myers equation is unique in that it gives the concentration as a function of capacity. There is no analytic solution for the capacity as a function of concentration, which is a major disadvantage. At low capacities, this equation reduces to Henry's law.

2.   Second Order Ln Polynomial Isotherm.

The logarithmic form of the Freundlich isotherm is

$$\ln(q) = \ln(K) + \eta \times \ln(c). \tag{I.5}$$

Thus, the Freundlich isotherm is a straight line when plotted on logarithmic axes. Static adsorption isotherms often show curvature when plotted on logarithmic axes. A 2nd order equation can show curvature; consequently, the following equation was determined empirically

$$\ln(q) = \ln(K) + \alpha \times \ln(c) + \beta \times \ln^2(c)$$
$$\text{or} \tag{I.6}$$
$$q = \exp\{\ln(K) + \alpha \times \ln(c) + \beta \times \ln^2(c)\}.$$

This equation (2nd ln poly) has been used extensively by our group to show isotherms over concentration ranges wider than can be represented by the normal Freundlich equation. This equation does not reduce to Henry's law at low concentration. This equation reaches a maximum at some concentration, then decreases for higher concentrations.

3.   Radke-Prausnitz Isotherm.

The Radke and Prausnitz (RP) equation is given by

$$q = \frac{\alpha \times \beta \times c^{\eta}}{\alpha + \beta \times c^{\eta-1}} \text{ or } \frac{1}{q} = \frac{1}{\alpha \times c} + \frac{1}{\beta \times c^{\eta}}. \tag{I.7}$$

At low concentrations, the RP equation reduces to Henry's law. At high concentration the capacity tends to infinity similarly to the Freundlich equation.

4.   Toth Isotherm.

The Toth equation is given by

$$q = q_{\infty} \times \frac{c}{(1 + \alpha \times c^{\eta})^{1/\eta}}. \tag{I.8}$$

At low concentrations, the Toth equation reduces to Henry's law. At high concentrations, the capacity approaches a finite capacity more slowly than the Langmuir isotherm.

5.   Dubinin-Astakov Isotherm.

Physical adsorption by microporous solids is often described by Dubinin's theory of micropore volume filling. The Dubinin-Astakov isotherm equation is given by

$$q = q_{\infty} \times \exp\left\{ -K \times \left(R \times T \times \ln\left(\frac{c_s}{c}\right)\right)^{\eta}\right\}$$
$$= q_{\infty} \times \exp\{-K \times A^{\eta}\} \tag{I.9}$$
$$= q_{\infty} \times \exp\left\{ -\left(\frac{A}{E}\right)^{\eta}\right\}$$

For many typical GACs, the exponent η is equal to 2, which corresponds to the original empirical equation postulated by Dubinin and Radushkevich in 1947. When the exponent η is equal to 1, the resulting equation is the Freundlich equation.

6.   Höll-Kirch Isotherm.

The Höll-Kirch (HK), or Langmuir-Freundlich, isotherm equation is given by

$$q = q_{\infty} \times \frac{K \times c^{\eta}}{1 + K \times c^{\eta}}$$
$$= q_{\infty} \times \frac{(K' \times c)^{\eta}}{1 + (K' \times c)^{\eta}} \tag{I.10}$$

At low concentrations, the HK equation reduces to the Freundlich equation. At high concentrations, the capacity approaches a finite capacity more slowly than the Langmuir isotherm.

C.   General Equations

Isotherms may be divided into two categories when considering the theory of adsorption onto heterogeneous solids. The first class is based on variants of the Langmuir isotherm, the second class is based on variants of the exponential isotherm.

1.   Marczewski and Jaroniec Isotherm.

The first category of heterogeneous isotherms is based on an assumption of a local Langmuir isotherm and a distribution of adsorption energies. An example of this class

is the Marczewski and Jaroniec (MJ) isotherm, otherwise known as the Generalized-Langmuir equation. This isotherm uses 4 parameters, and is given by

$$q = q_\infty \times \left(\frac{(K \times c)^\eta}{1 + (K \times c)^\eta} \right)^{\nu/\eta}. \quad \text{(I.11)}$$

This isotherm reduces to the Langmuir isotherm for $\eta = \nu = 1$, to the Höll-Kirch isotherm for $\eta = \nu$, and to the Toth isotherm for $\nu = 1$.

2. *Exponential Isotherm.* The second category of heterogeneous isotherms are based on the exponential isotherm (EI) equation. This is a very general equation and is given by

$$q = q_\infty \times \exp\left\{ -\sum_{i=1}^{n} K_i \times \left(R \times T \times \ln\left(\frac{c_s}{c}\right) \right)^i \right\}$$

$$= q_\infty \times \exp\left\{ -\sum_{i=1}^{n} K_i \times A^i \right\} \quad \text{(I.12)}$$

where n is the order of the equation. The total number of parameters is $n + 1$. This equation is equivalent to a nth order polynomial when the isotherm is plotted on logarithmic axes; consequently, this equation can express any isotherm if a sufficient number of terms are used.

Several common isotherm equations can be derived from the exponential isotherm equation. If $n = 1$, this equation reduces to the Freundlich equation. If $n = 2$, this equation is equivalent to the second order ln polynomial equation. If this equation is limited to a single term with an arbitrary exponent, this equation reduces to the Dubinin-Astakov equation.

7 Nomenclature

A Adsorption potential (J mol^{-1}) = $R \times T \times$ ln$\left(\frac{c_s}{c}\right)$.

BET   Brunauer-Emmett-Teller isotherm function, Eq. (I.3).

c Concentration (mg L^{-1})

c_s Solubility in water (1370 mg L^{-1} for TCE at 25°C (Riddick et al., 1986))

DA   Dubinin and Astakov isotherm function, Eq. (I.9).

E Characteristic energy (J mol^{-1}).

EI-n   n-th order exponential isotherm function, Eq. (I.12).

HK   Höll and Kirch isotherm function, Eq. (I.10).

K Strength of adsorption parameter (dimensions depend on equation).

m Adsorbent mass (g).

MJ   Marczewski and Jaroniec isotherm function, Eq. (I.11).

n Order of EI function.

q Adsorption capacity (mg g^{-1}).

q_∞ Maximum capacity at either infinite concentration or at the solubility limit (mg g^{-1}).

q_m Capacity at monolayer coverage (mg g^{-1}).

R Gas constant, 8.314510 J mol^{-1} K^{-1}

RP   Radke and Prausnitz isotherm function, Eq. (I.7).

Slope Slope of isotherm function (L g^{-1}).

T Temperature (K)

V Volume (L)

$X(A)$ Adsorption potential distribution (mol J^{-1}).

α_e Coefficient of thermal expansion (0.00115 for TCE at 25°C (Riddick et al., 1986))

α, β Heterogeneity or shape of isotherm parameters (dimensions depend on equation).

η, ν Exponent.

ΔH Differential molar enthalpy of adsorption (J mol^{-1}).

ΔS Differential molar entropy of adsorption (J mol^{-1} K^{-1}).

θ Relative adsorption or fraction of micropores filled (dimensionless).

σ Standard deviation of subscripted variable.

Notes

1. Ambersorb is a registered trademark of the Rohm and Haas Company, Philadelphia, PA.

2. Filtrasorb is a registered trademark of the Calgon Carbon Corporation, Pittsburgh, PA.

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