A Semi-Empirical Adsorption Equation for Single Component Gas-Solid Equilibria

A semi-empirical adsorption equation is derived and tested against published equilibrium sorption data on various types of systems. The equation is designed to satisfy the constraints imposed by the physics and the thermodynamics of the adsorption systems. It can describe the Type I and the Type III isotherms as well as their combinations. The model does not restrict the nature of the isosteric heat of adsorption to simplified forms such as a constant or a linear function of the surface coverage. This restriction is primarily responsible for limited applications of the published theories. Empirical equations relating the isosteric heat of adsorption and the surface excess variable are proposed.

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SCOPE

Analytical equations describing single component gas-solid adsorption equilibria are very useful to design engineers, particularly for modeling adsorption processes. Criteria for acceptable equations are:

(i) Adequate representation of the adsorption characteristics over the entire ranges of temperatures and pressures of interest.
(ii) Simple and explicit mathematical formulation using the least number of adjustable parameters for easy handling.

Numerous theories and semitheories describing pure gas adsorption isotherms are reported in the literature (Sing, 1973; Ponec etal, 1974) but their applications are often restricted to particular types of systems and to limited ranges of conditions. Some models do not even conform with the basic constraints imposed by physics. The primary reason of failure is the inability of the simplified models to simulate the very complex gas-solid and lateral molecular interactions which are responsible for the phenomenon of adsorption. Secondly, most models use a single, constant, monolayer or pore volume parameter to define the complicated adsorption space which severely distorts the actual situation. Finally, none of the published models deal with the Gibbs' excess, which is the true experimental variable for sorption systems. The actual amount adsorbed, which is the commonly used variable, is approximately equal to the Gibbs' excess only at low pressures. Failure to recognize this point alone may cause a model to be unsatisfactory in the high pressure region for some adsorbates. A list of common adsorption equations and their limitations is given in Table 1.

The purpose of this article is to propose a new semi-empirical adsorption equation for pure component gas-solid adsorption equilibria which does not suffer from some of the shortcomings mentioned above.

CONCLUSIONS AND SIGNIFICANCE

The proposed adsorption equations can be used to describe the Type I and the Type III isotherms as well as their combinations. The model shows that the isosteric heat of adsorption and its variation with the surface coverage constitute the key properties which determine the shapes of the isotherms for adsorption systems above the critical temperature of the sorbate. These properties can also describe the effects of a limited space in porous sorbents thereby eliminating the need for explicit definition of the adsorption space in terms of monolayer capacity or total pore volume. For systems below the critical temperature of the sorbate, the parameters of the equation are the isosteric heat of adsorption, the entropy of immersion and the limiting value of the surface excess variable at the saturation pressure. The last variable is meaningful only for the Type I systems. The entropy of immersion is important in establishing the Type II and the Type III shapes. The application of the proposed model is, however, limited to adsorbates whose isosteric heats are independent of temperature—a property valid for most systems.

The proposed empirical equations relating the isosteric heat of sorption and the surface excess variable are found to be adequate for describing various complex systems. However, that relationship is rather complicated. No general comments about the effect of the variation in the isosteric heat with surface coverage on the shapes of the isotherms can be made. The primary cause of limited application of most published theories is their inability to describe this complex property in a realistic fashion.

The principal significance of this work is that it provides a thermodynamically consistent analytic equation for describing equilibrium adsorption data over a wide range of temperatures and pressures. The same equation is applicable to various types of porous and non-porous sorbent-sorbate systems. Thus, the proposed model can be very useful to design engineers for data extrapolation, computation of multicomponent equilibria, and modeling adsorption processes.

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PROPERTIES OF ADSORPTION SYSTEMS

We first briefly review the various adsorption systems and their characteristics which must be satisfied by a model. We begin with the definition of Gibbs' surface excess (n^e), which is the pertinent experimental variable for describing the gas-solid equilibria. n^e is defined by:

$$n^e = V'(\rho' - \rho) \qquad (1)$$

where V' is the volume of the adsorbed phase per unit weight of the adsorbent, ρ' and ρ are, respectively, the molar densities of the adsorbed and the equilibrium bulk phases at the system temperature T and fugacity f. n^e is a function of f and T:

$$n^e = n^e(f, T) \qquad (2)$$

Clearly, n^e is approximately equal to $n'(=V'\rho')$, the actual amount adsorbed, only if $\rho' >> \rho$. This condition is satisfied in the low pressure region for most gas-solid systems. n^e deviates from n' as f increases. In fact, n^e can go through local maxima and minima at high pressures even though n' is a monotonically increasing function of f at constant T (Menon, 1968). In this study, we confine our discussions only to reversible adsorption systems and to the region where f is a single valued function of n^e.

There are three basic distinguishable shapes of the reversible adsorption isotherms. They are:

$$\left[\frac{\partial^2 n^e}{\partial f^2}\right]_T = 0 \qquad (3)$$

$$\left[\frac{\partial^2 n^e}{\partial f^2}\right]_T < 0 \qquad (4)$$

$$\left[\frac{\partial^2 n^e}{\partial f^2}\right]_T > 0 \qquad (5)$$

Equations 3 and 4 describe the characteristics of the Type I isotherms according to Brunauer classification (Brunauer etal, 1940). Type III isotherms are depicted by Eqs. 3 and 5. All other isotherms are combination of these two basic types. For example, Type II isotherms are typically Type I in the low pressure region and Type III in the high pressure region with a linear section in between (Eq. 3). The common features of all types of isotherms in the region of our interest are:

$$\left[\frac{\partial n^e}{\partial f}\right]_T > 0 \qquad (6)$$

$$\underset{f\to 0}{n^e} = Kf \qquad (7)$$

where K, a constant, is commonly known as the Henry's law constant. K is a function of temperature only. Equation 7 is derived from statistical mechanics (Hill, 1960) and it constitutes an important boundary condition for adsorption equations in the low pressure region.

The behavior of adsorption systems in the high pressure region is dictated by the temperature of the system. Typically, a Type I isotherm is exhibited if the temperature of the system is above the critical temperature of the adsorbate. In that case, there is no upper limit for values of n^e and f. All three types of isotherms are possible if the system temperature is below the critical temperature of the adsorbate. However, Type I isotherms are common for microporous adsorbents while Types II and III or other combinations of Types I and III are exhibited by the non-porous adsorbents. In summary, the boundary conditions imposed by the temperature of the system are:

$$T > T_c\text{: Type I Isotherm, No Upper Bound for } n^e \text{ or } f \qquad (8)$$

$$T < T_c\text{: Type I Isotherm, } n^e \to \text{ Finite As } f \to f^s \qquad (9)$$

$$\text{Types II and III Isotherms, } n^e \to \text{ Infinite as } f \to f^s \qquad (10)$$

where T_c is the critical temperature of the adsorbate and f^s is the fugacity of the adsorbate corresponding to its vapor pressure at the temperature of the system. f^s also represents the upper limit for the f variable in Eq. 2 for systems below the critical temperature of the adsorbate.

Equations 2-10 describe the basic properties of different adsorption systems and, therefore, an acceptable model must have the capability to depict all those features. In addition, the thermodynamics of adsorption imposes additional constraints on the adsorption equations which are discussed below.

THERMODYNAMIC CONSTRAINTS

The key thermodynamic variables for describing single component adsorption equilibria are:

$$g^e = -RT\int_0^f n^e \cdot d\ln f \quad \text{Constant } T \qquad (11)$$

$$h^e = -\int_0^{n^e} q\,dn^e \qquad (12)$$

$$g^e = h^e - TS^e \qquad (13)$$

$$q = RT^2 \cdot \left[\frac{\partial \ln f}{\partial T}\right]_{n^e} \qquad (14)$$

where g^e, h^e and s^e are, respectively, the excess free energy, the excess enthalpy and the excess entropy of the adsorption system. q is the isosteric heat of adsorption defined by Eq. 14. All excess properties can be calculated using experimental adsorption equilibria at different temperatures in conjunction with Eqs. 11-14.

The limiting values of q and the excess properties in the low pressure region can be obtained by combining Eq. 7 with Eqs. 11-14. Thus, one gets:

$$\underset{f\to 0}{g^e} = -n^e RT \qquad (15)$$

$$\left(\frac{\partial g^e}{\partial T}\right)_{\substack{n^e \\ f\to 0}} = -n^e R \qquad (16)$$

$$\underset{f\to 0}{q} = q^0 = -RT^2 \cdot \left[\frac{d\ln K}{dT}\right] \qquad (17)$$

$$\left[\frac{dq}{dn^e}\right]_{\substack{T \\ f\to 0}} = 0 \qquad (18)$$

where q^0, a constant, is the isosteric heat of adsorption at the limit of zero coverage.

The upper bounds on the excess properties are governed by the temperature of the system. For $T < T_c$,

$$\underset{f\to f^s}{g^e} = g^* \qquad (19)$$

$$\left(\frac{\partial g^e}{\partial T}\right)_{\substack{n^e \\ f\to f^s}} = -s^* \qquad (20)$$

$$\int_0^{n^e} (q - L)dn^e = -h^* \qquad (21)$$

where g^*, s^* and h^* are finite quantities, representing respectively, the pure liquid free energy of immersion, the entropy of immersion and the heat of immersion for the adsorbate at the temperature of the system. L is the latent heat of vaporization of the adsorbate at the temperature of the system. Equations 19-21 are obtained from the thermodynamic analogy between adsorption from vapors and adsorption from liquids (Myers and Sircar, 1972b). For $T > T_c$, there are no constraints for the upper limits of g^e or its temperature coefficient.

Other limiting conditions imposed by the thermodynamic analogy between adsorption from vapors and liquids for Type II and Type III systems are as follows:

$$q_{f\to f^s} = L \tag{22}$$

$$\left(\frac{\partial q}{\partial n^e}\right)_{\substack{T\\ f\to f^s}} = 0 \tag{23}$$

L also represents the minimum value of q for most adsorption systems because the adsorbed phase is seldom denser than the liquid. Thus,

$$q \geqq L \tag{24}$$

Validity of Eqs. 22-24 can be demonstrated by integrating the left hand side of Eq. 21 by parts and using Eq. 10.

DERIVATION OF ADSORPTION EQUATION

We now proceed to derive an adsorption equation that satisfies the properties of the adsorption systems outlined above. As mentioned earlier, the molecular interactions are key to the description of adsorption characteristics. That information is implicitly provided by the isosteric heat of adsorption which can either be evaluated from adsorption isotherms using Eq. 14 or be measured calorimetrically (Ponec, et al., 1974). The isosteric heat of adsorption is commonly found to be independent of temperature for most systems over a wide range of temperatures. This property allows us to integrate Eq. 14 at a constant n^e to obtain,

$$\ln f = -q/RT + F(n^e) \tag{25}$$

Both q and F in Eq. 25 are functions of n^e. Equations 11 and 25 can be combined to get,

$$g^e = \int_0^{n^e} n^e dq - RT\int_0^{n^e} n^e \cdot \left(\frac{dF}{dn^e}\right)\cdot dn^e \tag{26}$$

$$\left[\frac{\partial g^e}{\partial T}\right]_{n^e} = -R\int_0^{n^e} n^e \cdot \left(\frac{dF}{dn^e}\right)\cdot dn^e \tag{27}$$

Equation 27 shows that a priori knowledge of the temperature coefficient of the free energy excess will define the nature of the function F which can then be substituted into Eq. 25 to obtain an adsorption equation. However, the only known information about the temperature coefficient of g^e are its boundary values as given by Eqs. 16 and 20. Here we propose a simple mathematical form that satisfies those equations in view of Eqs. 9 and 10:

$$\left(\frac{\partial g^e}{\partial T}\right)_{n^e} = -\frac{Rn^e}{1 + bn^e} \tag{28}$$

where

$$b = \frac{R}{s^*} - \frac{1}{n^*} \tag{29}$$

n^* is the limiting value of n^e at $f = f^s$. For the Type II and III systems, Eq. 29 becomes:

$$b = R/s^* \tag{30}$$

Equation 28 is empirical but it satisfies the properties of the adsorption systems at $T < T_c$. We assume that Eq. 28 also represents the form of the temperature coefficient of g^e for systems at $T > T_c$. In that case, b can be treated as an empirical constant. The form reduces to the actual value of the property only at low coverages (Eq. 16).

Equations 25, 27 and 28 can be combined to obtain the following adsorption equation,

$$\ln f = -\frac{q}{RT} + \ln\left[\frac{n^e}{1 + bn^e}\right]e^{\left[\frac{1}{1 + bn^e}\right]} + C_o \tag{31}$$

where C_o is an integration constant.

Equation 31 reduces to the linear form of Eq. 7 in the Henry's law region as follows:

$$n^e_{f\to 0} = e^{-(C_o+1)}\, e^{q_o/RT} \cdot f \tag{32}$$

Equation 32 describes the physical significance of the constant C_o in relation to the Henry's law constant K.

An alternate form of Eq. 31 applicable to systems below T_c may be derived by combining it with Eq. 22:

$$\ln\frac{f}{f^s} = -\frac{(q - L)}{RT} + \ln\left[\frac{an^e}{1 + bn^e}\right]\cdot e^{\left[\frac{1}{1+bn^e}\right]} \tag{33}$$

where

$$\ln a = -\ln\left[\frac{s^*}{R}\right]e^{s^*/Rn^*} \text{ for Type I Systems} \tag{34}$$

and

$$a = b = R/s^* \text{ for Type II and III Systems} \tag{35}$$

Equations 31 and 33 are the proposed adsorption equations. They can be used to fit experimental adsorption data provided isotherms at two or more different temperatures are available for the system of interest. Such data are needed for defining q. Alternately, calorimetrically measured values of q at different values of n^e can be used. The absence of this information prevents complete description of the adsorption characteristics. This is demonstrated by the fact that many adsorption equations are capable of representing the equilibrium data at one temperature for a system but a poor fit is often realized when isotherms at different temperatures are tested simultaneously. Equations 31 and 33, therefore, offer an important improvement over many published isotherms since they do not restrict the functional dependence of q on n^e to a constant value or to some other simplified forms (Table 1).

FORM OF q

Clearly, an analytic function relating q and n^e is needed before Eqs. 31 and 33 can be used to fit experimental data. Here, we propose two simple functional forms:

$$(q - L) = (q_o - L)e^{-\sum_{k=2}^{k=N} \beta_k (n^e)^k} \quad \text{For } T < T_c \tag{36}$$

$$q = q_o e^{-\sum_{k=2}^{k=N} \beta_k (n^e)^k} \quad \text{For } T > T_c \tag{37}$$

where $\beta_k(k = 2, 3, \ldots . N)$ are empirical constants. Equations 36 and 37 satisfy the relevant constraints on q imposed by Eqs. 17, 18, 22, 23 and 24. The polynomials are designed to start from $k = 2$ in order to satisfy constraint (Eq. 18).

The expressions given by Eqs. 36 and 37 are very flexible. A variety of shapes for q as a function of n^e can be generated by using only a few terms of the polynomial. Figure 1 shows some of the typical shapes of q. Curves a and b are common for the Type I isotherms, while curves c-g are exhibited by the Type II and III isotherms (Ponec et al., 1974). Local maxima and minima in q can be obtained at the roots of the following equation:

$$\sum_{k=2}^{k=N} k\beta_k(n^e)^{k-1} = 0 \tag{38}$$

TEST OF ADSORPTION EQUATIONS

The applicability of the adsorption Eqs. 31 and 33 in conjunction with Eqs. 36 and 37 was evaluated using published experimental adsorption data on various types of systems. Table 2 describes the different systems tested along with the values of the "best fit parameters" of the adsorption equations. They were

TABLE 1. COMMON ADSORPTION EQUATIONS AND THEIR LIMITATIONS

Name	Adsorption Equation	Types of Isotherms That can be Described	Isotherm Satisfies Eq. 7	Isotherm Satisfies Eq. 19	Form of q Derived from the Isotherm
Freundlich:	$\theta = C\, P^k$	Type I Only for $k < 1$ Type III Only for $k > 1$	No	g^* Not Defined	$q(n^e) = \text{Constant}$
Langmuir:	$\theta = \frac{CP}{1 + CP}$	Type I Only	Yes	Asymptotically	$q(n^e) = \text{Constant}$
Volmar:	$P = \frac{k\theta}{1-\theta}\, e^{\theta(1-\theta)}$	Type I Only	Yes	Asymptotically	$q(n^e) = \text{Constant}$
Fowler-Guggenheim:	$P = \frac{k\theta}{1-\theta}\, e^{(-C\theta)}$	Types I or III Below $\theta = 0.5$ Type I Only Above $\theta = 0.5$	Yes	Asymptotically	$q(n^e) = c_1 + c_2\theta$
Hill-deBoer:	$P = \frac{k\theta}{1-\theta}\, e^{\left[\frac{\theta}{1-\theta} - C\theta\right]}$	Types I or III Below $\theta = 0.33$ Type I Only Above $\theta = 0.33$	Yes	Asymptotically	$q(n^e) = c_1 + c_2\theta$
Temkin:	$P = ke^{\theta}$	Type I Only	No	g^* Not Defined	$q(n^e) = \text{Constant}$
Brunauer-Emmett-Teller:	$\theta = \frac{cx}{(1-x)[1 + (C-1)x]}$	Types II and III Only	Yes	g^* Not Defined	$q - L = -\frac{C_1(1-x)^2}{[1 + (C-1)x^2]}$
Frenkel-Halsey-Hill:	$\ln x = -\frac{C}{\theta^k}$	Types II and III Only	No	g^* Not Defined	$q - L = \text{Constant}$
Dubinin-Kaganer:	$\ln\theta = C(\ln x)^2$	Type III Only at Low θ Type I Only at Large θ	No	g^* Not Defined	$q - L = c_1 (\log\theta)^{1/2}$
	$\ln\theta = C(\ln x)$	Type I Only if $C < 1$ Type III only if $C > 1$	No	Yes	$q - L = c_1 \log\theta$
Empirical:	$\theta = \frac{(CP)^k}{1 + (CP)^k}$	Type I Only for $k < 1$	No		$q = c_1 + c_2 \log\left[\frac{\theta}{1-\theta}\right]$

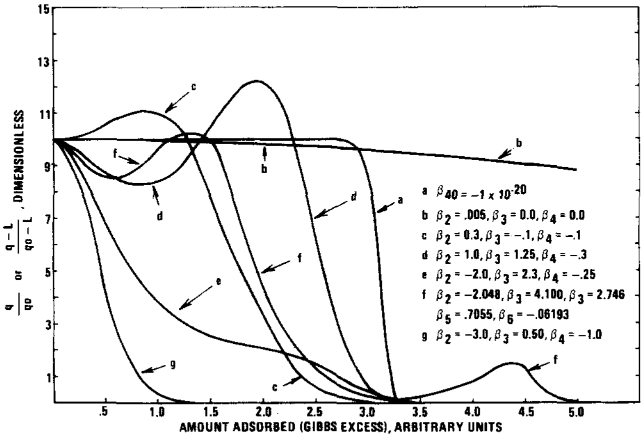

Figure 1. Flexibility of Eqs. 36 and 37 for generating q vs. n^e plots.

obtained by using a least square search technique. Figures 2-8 show the results of the test. Figure 9 shows the variation in q as a function of n^e. A discussion of the results follows:

System I—Methane on Activated Carbon (Reich, 1974)

The adsorbent is the highly porous BPL activated carbon produced by Pittsburg Activated Carbon Company. Approximately 60% of its pore volume is contained in the pores below 30Å in diameter while the remainder of the pores are in the macropore region of diameters greater than 100Å. The system temperatures are above the critical temperature of methane and the isotherms are Type I in shape. Figure 2 shows the best fit of the experimental data using Eq. 31 and five terms of the q polynomial in Eq. 37. The fit is almost quantitative in the entire fugacity (0-34 atm.) and temperature (−60°-+28°C) ranges of the data. The isosteric heat of adsorption is found to decrease monotonically as n^e increases.

TABLE 2. BEST FIT PARAMETERS OF THE ADSORPTION EQUATIONS

Systems	b*	$Co = \ln a$**	q^0 or $(q^0 - L)$***	Parameters of q Polynomial**** $\beta 2$	$\beta 3$	$\beta 4$	$\beta 5$	$\beta 6$
I. Methane on Activated Carbon	0.0	7.327	4.762	−0.06912	0.04024	−0.01117	0.00144	−0.0000698
II. Ethane on Activated Carbon	0.0	11.650	7.677	−0.13270	0.08390	−0.02221	0.00262	−0.0001138
III. Benzene on Silica Gel	0.0	2.576	5.612	−0.39700	0.47010	−0.25180	0.06283	−0.0059140
IV. Carbon Dioxide on NaX Zeolite	0.0	257.020	11.020	−0.04365	0.01443	−0.00156		
V. Ethylene on Graphitized Thermal Carbon Black	0.0703		1.511	0.00966	−0.00574	0.00157	−0.00024	0.0000110
VI. Methanol on Graphitized Thermal Carbon Black	0.8052		0.773	0.00181	−0.00059	0.000009		
VII. Benzene on Graphitized Thermal Carbon Black	0.0433		1.986	−0.13310	0.05837	−0.009268		

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* Units of b are $(\text{mmol/g})^{-1}$ for systems I-IV and $(\mu\text{mol/m}^2)^{-1}$ for systems V-VII.
** Units of a are $(\text{mmol/g})^{-1}$ for systems I-IV.
*** Units of q^0 or $(q^0 - L)$ for kcal/mol for all systems.
**** Units of β_k are $(\text{mmol/g})^{-k}$ for systems I-IV and $(\mu\text{mol/m}^2)^{-k}$ for systems V-VII.

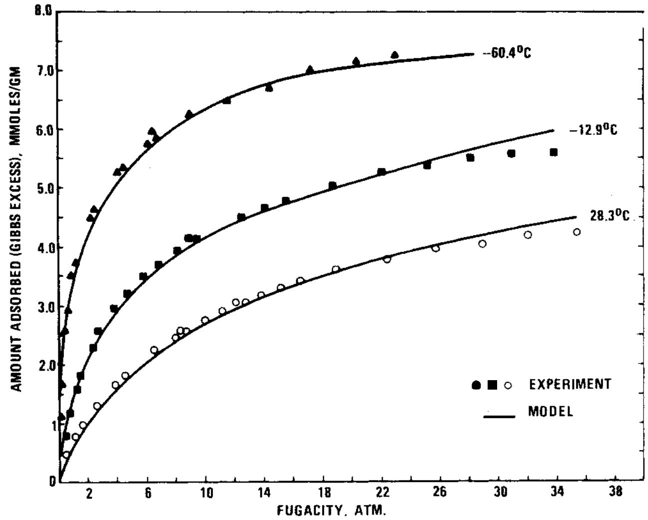

Figure 2. Adsorption of methane on activated carbon.

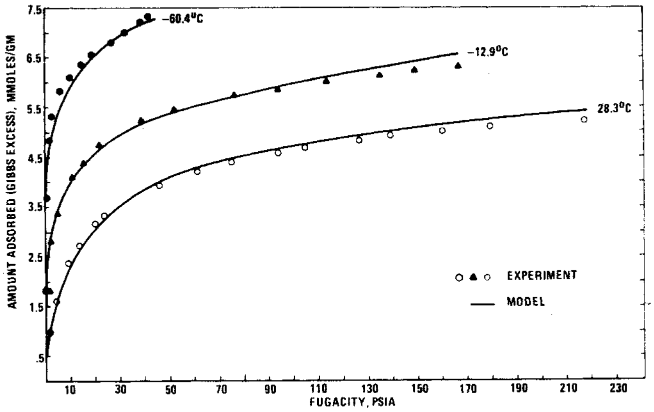

Figure 3. Adsorption of ethane on activated carbon.

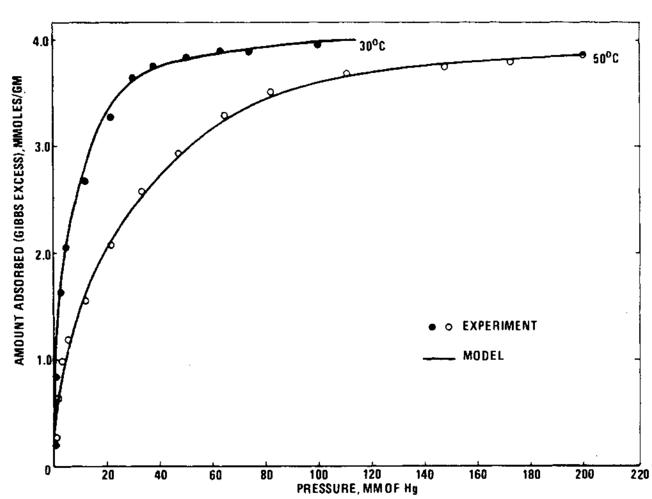

Figure 4. Adsorption of benzene on silica gel.

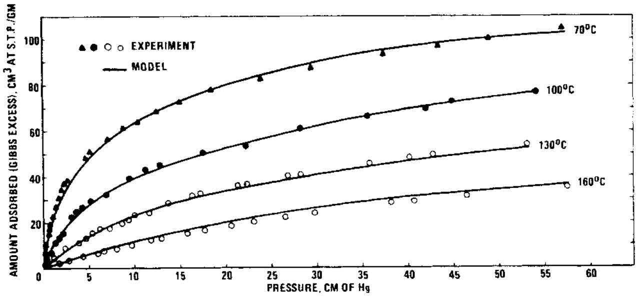

Figure 5. Adsorption of carbon dioxide on NaX zeolite.

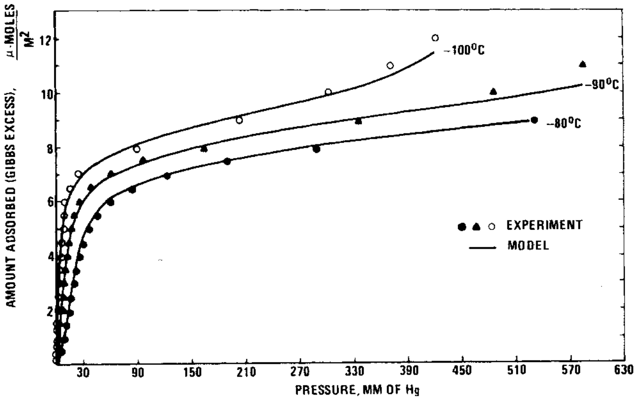

Figure 6. Adsorption of ethylene on graphitized thermal carbon black.

System II—Ethane on Activated Carbon (Reich, 1974)

The carbon and the isotherm temperatures for this system are the same as those of system I. However, the temperatures in this case are below the critical temperature of ethane. The isotherms are Type I in the region of the data. Figure 3 shows the best fit of the data using Eq. 33 and five terms of the polynomial in Eq. 36. q is again found to be a monotonically decreasing function of n^e.

System III—Benzene on Silica Gel (Myers and Sircar, 1972a)

The gel is grade PA 400 produced by W. R. Grace and Company. The nominal pore diameter is 22Å. The system temperatures are below the critical temperatures of benzene and the isotherms are Type I. Figure 4 shows the best fit of the experimental data by Eq. 33. Again five terms of the q polynomial are needed. q for this system decreases slowly with increasing n^e until its saturation limit is reached, then q drops very rapidly to the latent heat of vaporization of benzene.

System IV—Carbon Dioxide on NaX Zeolite (Barrer and Coughlan, 1968)

The adsorbent is manufactured by Union Carbide Corporation and is truly microporous with an average pore diameter of 10Å. The system temperatures are above the critical temperature of carbon dioxide and the isotherms are Type I. A near quantitative fit of the data is obtained by using Eq. 31 and three terms of the q polynomial as shown in Figure 5. The isosteric heat of adsorption is found to decrease with increased coverage. q^0 for this system is very large (~11 kcal/mol) which is responsible for the early "knee bend" of the isotherms.

Systems V to VIII—Ethylene, Methanol and Benzene on Graphitized Thermal Carbon Black (Avgul and Kiselev, 1970)

The adsorbents for these systems are nonporous thermal carbon blacks. The system temperatures are below the critical temperatures of the adsorbates.

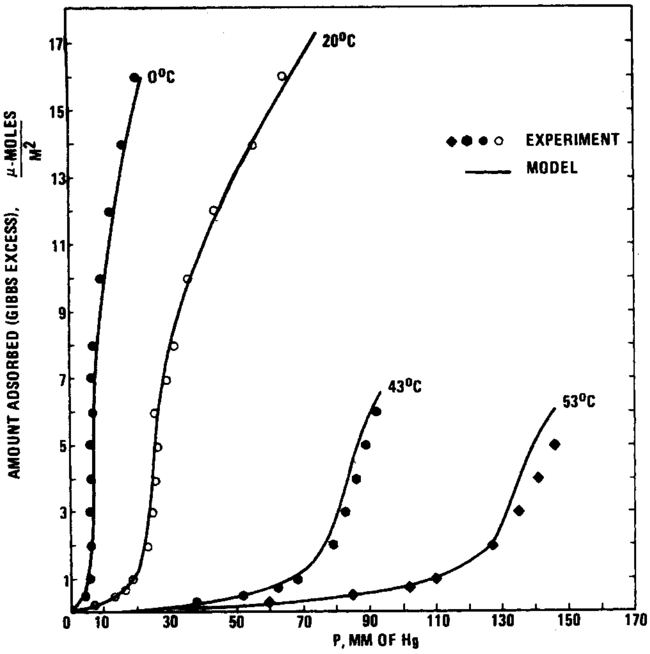

Figure 7. Adsorption of methanol on graphitized thermal carbon black.

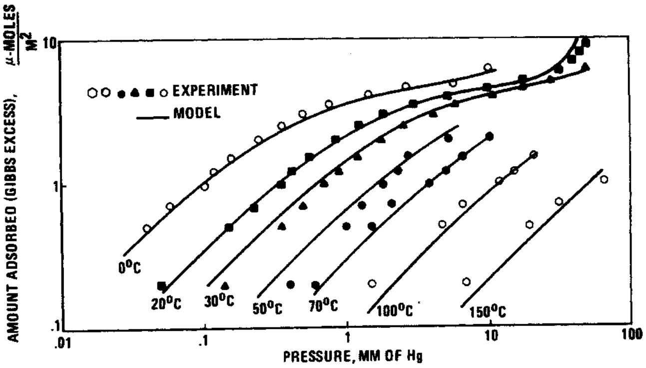

Figure 8. Adsorption of benzene on graphitized thermal carbon black.

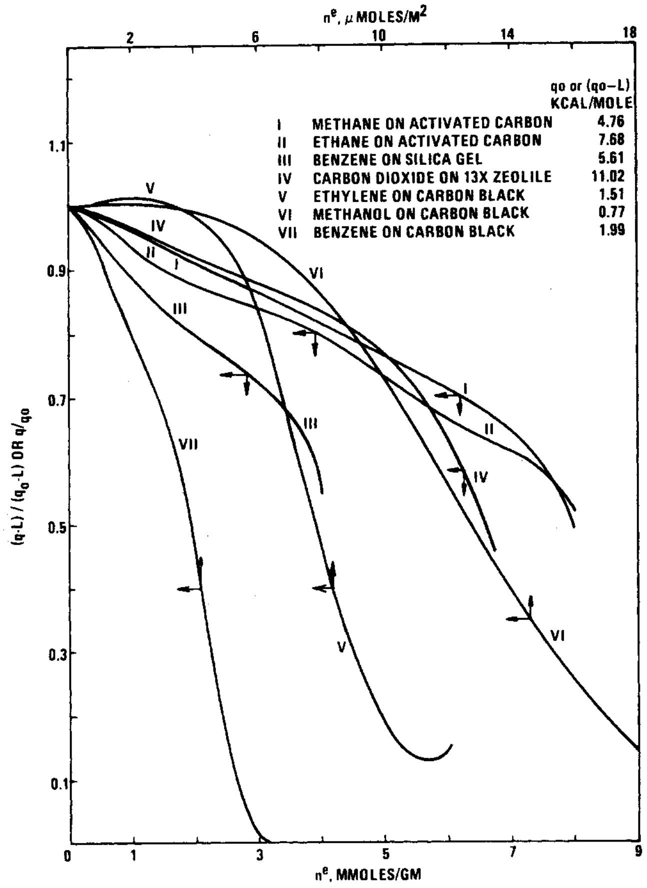

Figure 9. Isosteric heats of adsorption as a function of the surface excess.

The ethylene-carbon black system exhibits Type III behavior in the low and the high pressure regions with an intermediate section of Type I. Figure 6 shows the best fit of the data using Eq. 33 and five terms in the polynomial of Eq. 37. q for the system first increases with increased coverage and then it rapidly drops. Finally, it goes through a local minima and a maxima at high coverages.

The methanol-carbon black system is type III in the region of the data shown in Figure 7. Equation 33 fits the data very well using three terms of the q polynomial. q for this system remains almost constant up to a certain coverage in the low pressure region and then it drops slowly to the latent heat of vaporization of methanol.

The isotherms for the benzene-carbon black system belong to Type II. The data shown in Figure 8 are measured by different workers using carbon blacks of different surface areas. It is assumed that the chemical natures of the carbon blacks are the same and the data can be unified by plotting n^e as the amount per unit area of the adsorbent. It can be seen from Figure 8 that Eq. 33 in conjunction with three terms of the q polynomial fits the data very well. The value of q decreases rapidly with increasing n^e and becomes equal to the latent heat of vaporization of benzene in the high pressure region where the isotherms assume Type III form.

It should be evident from above results that Eqs. 31 and 33 are capable of describing equilibrium adsorption data for various types of systems over a wide range of temperatures and pressures. This indicates that the assumed form of the temperature coefficient of excess free energy (Eq. 28) is acceptable. It also shows that the proposed relationships between the isosteric heat of adsorption and the surface excess variable (Eqs. 36 and 37) are satisfactory.

SOME PROPERTIES OF PROPOSED ADSORPTION EQUATIONS

Parameters of Equations

The key parameters of the proposed adsorption equation for systems above the critical temperature of the sorbate (Eq. 31) are the isosteric heat of adsorption (q), the empirical constant b and the constant C_o which is related to the Henry's law constant. The equation does not contain any parameter such as the monolayer capacity or the adsorbent pore volume which are commonly used to define the adsorption space. Thus the model shows that the isosteric heat of adsorption and its variation with the surface coverage are primarily responsible in determining the shape of the isotherms. The effects of the limited adsorption space for porous adsorbents are manifested in the variation of q with n^e. The very complex nature of the relationship between q and n^e, however, prevents any generalization about its effects on the shape of an isotherm. Nevertheless, it can be shown using Eqs. 31 and 37 that larger values of q^0 will cause earlier knee bends in Type I isotherms.

The adsorption equation for systems below the critical temperature of the sorbate (Eq. 33) contain the isosteric heat of adsorption (q), the entropy of immersion (s^*) and the limiting value of the surface excess (n^*) as the key parameters. The variation of q with n^e again plays an important and complex role in determining the shapes of the isotherms.

The role of the parameter s^* is crucial in establishing the shapes of Type II and Type III isotherms. It can be shown that non-zero values of the parameter b, which is inversely proportional to s^*, is primarily responsible for generating an isotherm characteristic of Type III described by Eq. 5.

The parameter n^* is meaningful only for Type I systems. Its value tends to infinity for Types II and III systems. It is, however, possible that the Type I isotherms for $T < T_c$ are actually Type II in shape with n^* approaching infinity as $f \rightarrow f^s$ preceded by a long plateau extending almost to the point of the saturation pressure. In that case, only Eqs. 33 and 35 are needed to describe all types of adsorption systems below T_c without defining an adsorption space parameter. Lack of good experimental data and difficulty of sorption measurements in the region of interest, however, makes the concept almost impossible to verify.

Boundary Conditions

An important property of the proposed adsorption equations and the proposed relationship between q and n^e is that they satisfy the appropriate limiting conditions described by the Eqs. 7-10 and the Eqs. 15-24. These constraints are imposed either by the physics or the thermodynamics of the adsorption systems. This property permits the proposed model to be used for data extrapolation to the very low pressure region or to the limit of saturation pressure. Such extrapolation cannot be carried out using many of the published theories because they do not satisfy the necessary constraints (Table 1).

Relationship with the Virial Equation of State

It may be interesting to note that the "best fit" value of the parameter b in Eqs. 31 and 33 for Type I systems evaluated in this work is equal to zero. This property reduces those two equations to the following form:

$$\ln f = -\frac{q}{RT} + \ln n^e + A_0 \tag{39}$$

where A_0 is a constant. It will be shown below that Eq. 39 represents a special case of the adsorption equation derived from the two dimensional virial equation of state (Sing, 1973). The virial adsorption equation may be written as:

$$f = n' e^{\sum_{k=1} B_k (n')^{k-1}} \tag{40}$$

where B_k (k = 1, 2, 3, . .) are functions of temperature only. Equation 40 uses n', the actual amount adsorbed, as the variable representing the extent of adsorption. One can combine Eq. 40 with Eq. 14 and obtain the following expressions for q and B_k by using the assumption that q is independent of temperature:

$$q = \sum_{k=1} \alpha_k (n')^{k-1} \tag{41}$$

$$B_k = -\frac{\alpha_k}{RT} + \epsilon_k \tag{42}$$

where α_k and ϵ_k are constants. Equation 40 can then be rewritten in the form:

$$\ln f = -\frac{q}{RT} + \ln n' + \sum_{k=1} \epsilon_k (n')^{k-1} \tag{43}$$

Equation 43 reduces to the form of Eq. 39 if the constants ϵ_k for $k > 1$ are equal to zero. This indicates that the virial equation of state is a special case of the adsorption equation proposed in this article.

NOTATION

a = constant defined by Eqs. 31 and 33
A_0 = constant defined by Eq. 39
b = constant defined by Eqs. 29 and 30
B_k = function of temperature only
c = function of temperature only
c_i = constants independent of temperature
C_o = constant defined by Eqs. 31 and 32
f = gas phase fugacity
f^s = fugacity at saturation pressure
F = function of n^e only defined by Eq. 25
g^e = excess free energy of adsorption
g^* = free energy of immersion
h^e = excess enthalpy of adsorption
h^* = enthalpy of immersion
k = functions of temperature only
K = Henry's law constant defined by Eq. 7
L = latent heat of vaporization
m = monolayer capacity
n' = amount adsorbed
n^e = surface excess
n^* = surface excess at saturation
P = gas phase pressure
P^s = saturation pressure
q = isosteric heat of adsorption
q^0 = isosteric heat of adsorption at zero coverage
R = gas constant
s^e = excess entropy of adsorption
s^* = entropy of immersion
T = temperature
T_c = critical temperature
V' = adsorbed phase volume
x = relative pressure, P/P^s

Greek Letters

α_k = constants independent of temperature
β_k = constants independent of temperature
ϵ_k = constants independent of temperature
ρ = molar density of gas phase
ρ' = molar density of adsorbed phase
θ = fractional coverage, n'/m

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