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Sorption of Polar Vapors on Elastic Wall Gels

Paul Fugassi and George Ostapchenko

Coal Research Laboratory, Dept. of Chemistry
Carnegie Inst. of Technology, Pittsburgh 13, Pa.

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$$W_c = \frac{AK\Sigma}{1 + K\Sigma}$$

$$\Sigma = \frac{K_1 p^0 c}{(1 + (K_1 p^0 - 1)c)(1 - c)}$$

In these equations, W_c is the sorption usually expressed as moles of sorbed vapor per gram of solid, c is the relative pressure of the vapor and p^0 is the vapor pressure of the liquified vapor at the temperature in question. The equation has three adjustable parameters; A , K , and K_1 .

The equation has been applied to the sorption of polar vapors by proteins, nylon and other gels of the elastic wall type. The equation agrees with experiment over a range of relative pressures from 0.1 to 0.9, and also accounts for the effect of temperature changes.

Since the equation was developed on the assumption that surface adsorption is negligible relative to interior absorption, it would appear that sorption of polar vapors by elastic wall gels of the protein and polysaccharide is mainly a solution process.

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Coal Research Laboratory, Dept. of Chemistry
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Summary

From an investigation of the kinetics of methanol sorption on coal, a new sorption isotherm has been derived of the form,

$$W_e = \frac{AK\Sigma}{1+K\Sigma}, \quad \Sigma = \frac{\pi_1 p^0 c}{(1 + (\pi_1 p^0 - 1)c)(1-c)}$$

In these equations, W_e is the sorption usually expressed as moles of sorbed vapor per gram of solid, c is the relative pressure of the vapor and p^0 is the vapor pressure of the liquefied vapor at the temperature in question. The equation has three adjustable parameters, A , K , and K_1 .

The equation has been applied to the sorption of polar vapors by proteins, nylon and other gels of the elastic wall type. The equation agrees with experiment over a range of relative pressures from 0.1 to 0.9 and also accounts for the effect of temperature changes.

Since the equation was developed on the assumption that surface adsorption is negligible relative to interior absorption, it would appear that sorption of polar vapors by elastic wall gels of the protein and polysaccharide types is mainly a solution process.

Introduction

Recent kinetic investigations made in this laboratory on the sorption of gaseous methanol by coal(1) and cellulose(2) have shown that both coal and

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1. P. Fugassi, G. Ostapchenko, and R. Trammell, Fuel
 2. P. Fugassi and G. Ostapchenko,
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cellulose follow the same rate equation,

$$W = \frac{k_x W_e^2 t}{1 + k_x W_e t}$$

In this equation W is the weight of alcohol taken up by one gram of solid at time t , W_e is the corresponding weight at infinite time, t is the time and k_x is the experimental velocity constant. On the basis of fragmentary data in the literature and unpublished data from this laboratory it appears that a rate equation of this form would be expected if the gas is a polar compound and if the solid is an elastic wall gel composed of oxygen containing compounds.

For methanol sorption on cellulose the experimental velocity constant involves the fraction of surface sites holding two methanol molecules per site and from this fact the adsorption of methanol on the surface of cellulose is

known to be of the multilayer type. The dependence of k_x upon the surface sites holding two methanol molecules gave a new sorption equilibrium isotherm of the following type.

$$W_e = \frac{AK\Sigma}{1+K\Sigma} \quad (1)$$

$$\Sigma = \frac{K_1 p^0 c}{(1 + (K_1 p^0 - 1)c)(1-c)} \quad (2)$$

In equation 1, W_e is the equilibrium sorption in moles per gram of solid at some fixed temperature, A is a constant being moles of interior sites per gram of solid, and K is a dimensionless equilibrium constant. In equation 2, K_1 is an equilibrium constant (atm.^{-1}) for the adsorption of methanol on surface sites, p^0 is the vapor pressure (atm.) of the liquefied vapor at the temperature in question, and c is the relative pressure of the vapor.

The mechanism which leads to these equations is that vapor is rapidly adsorbed on the surface sites and then adsorbed molecules slowly migrate from the surface into the solid phase.

Equation 1 really gives the amount of vapor dissolved in the solid. The total amount of vapor held by the solid is obviously the sum of two terms; the adsorption on the surface and the absorption in the interior. Thus,

$$(W_e)_{\text{total}} = (W_e)_{\text{interior}} + (W_e)_{\text{surface}}$$

For the total amount of vapor held by the solid, which is the experimental quantity measured, the full equation is,

$$(W_e)_{\text{total}} = \frac{AK\Sigma}{1+K\Sigma} + Bf(c) \quad (3)$$

In equation 3, B represents moles of surface sites per gram of solid.

The nature of $f(c)$ is not completely known. If $f(c)$ is Σ , the full equation would have four parameters; A , B , K_1 and K . However, Σ is really the BET equation for an infinite number of layers and approaches infinity as c approaches 1. For this reason $f(c)$ must be a modified BET equation where adsorption is restricted to n layers. The use of a modified BET equation introduces five parameters and this number of parameters is meaningless when only equilibrium data are available. Kinetic data if available would permit independent evaluation of one of the parameters. However such data are not available for most of the systems to be discussed here.

In applying the full equation (3) to the data in the literature the assumption will be made that B approaches zero. Experimentally there is evidence that in the case of methanol sorption on cellulose this assumption is valid. In this case the amount of methanol adsorption on the surface appears to be less than ten percent of the total weight of methanol held by the cellulose. However an assumption of this type would be expected to effect the behavior of the equation at low values of c . Accordingly the discussion which follows uses the partial equation (1) and is limited to a range of relative pressures from 0.1 to higher values. Equation 1 will be applied to some of the data available in the literature on the sorption of polar molecules by elastic wall gels.

Sorption of Water by Proteins

A comprehensive study of water sorption by various proteins has been published by Bull(3). He showed that the experimental data fitted the BET

3. H. B. Bull, J. Am. Chem. Soc., 66, 1499 (1944)

equation up to relative pressures of 0.4-0.5 excepting salmin where two different sets of constants in the BET equation were required. In general application of the new equation shows that the experimental data are followed up to relative pressures of 0.9 or greater. A comparison of experimental and calculated values of W_e for the sorption of water on wool are given in Table I.

Table I
Calculated and Experimental Values W_e - Water on Wool

c	$W_e \times 10^3$ (expt.)	$W_e \times 10^3$ (calc.)	W_e (calc. - expt.)
0.1	2.36 moles/gram	2.06 moles/gram	-0.3 moles/gram
0.2	3.47	3.56	+0.09
0.3	4.57	4.54	-0.03
0.5	6.35	6.38	+0.03
0.7	8.67	8.71	+0.04
0.9	12.52	12.46	-0.06

As previously mentioned the use of equation 3 would give better agreement at low values of c.

Equation 1 has three parameters; A, K, and K_1 . A tabulation of the values of these parameters for the sorption of water on various proteins is given in Table II.

Table II
Sorption of Water on Proteins (3)

Protein	K_1 (atm. ⁻¹)		K		A (moles sites/gram)	
	25°C.	40°C.	25°C.	40°C.	25°C.	40°C.
Wool	173.18	65.02	0.4133	0.4346	0.0155	0.0144
Salmin	228.23	155.70	-.0052	-.0232	.8334	.1669
Gelatin	280.32	89.22	.2500	.3286	.0289	.0239
Collagen	315.56	85.04	.2473	.3057	.0317	.0273
β -Lactoglobulin (crystals)	182.67	71.99	.2117	.2157	.0240	.0225
Silk	213.53	80.03	.2772	.3038	.0127	.0113
C-Zein	305.67	114.72	.1842	.2401	.0148	.0118
B-Zein	283.47	132.86	.2308	.2363	.0128	.0115

The values of the equilibrium constant, K_1 , in Table II are for the reaction, $H_2O(g) + S \rightleftharpoons S \cdot H_2O$. In this equation S represents surface sites. It will be noted that K_1 always decreases as temperature increases. The heat of reaction associated with the change in K_1 can be calculated by conventional methods. When this is done it is found that the calculated heats of reaction range from 9,400 to 16,200 cal. per mole excluding salmin, and the average value is about 12,000 cal. per mole. It appears that the surface sites on various proteins are very similar as would be guessed from their similar chemical composition.

The values of K in Table II are for the reaction, H_2O (surface) + D \rightleftharpoons D \cdot H_2O . Here D represents interior sites. An increase in temperature gives an increase in K. However the change is not great so that the heat of reaction is close to zero or in the extreme case about 3,000 cal. per mole endothermic. The values of K for salmin are negative which is an impossibility. The behavior of salmin is stated by Bull(3) to be different from that of the other proteins. Salmin dissolves at a relative pressure of 0.7 and while for

the other proteins the BET equation is followed to a relative pressure of 0.5, for salmin two BET equations are needed. Pauling(4) suggested that for salmin

 L. L. Pauling, J. Am. Chem. Soc., 67, 555 (1945)

the number of sites increased with increasing sorption of water. The negative values for K could either be blamed on experimental errors in which case the true value of K is a small positive number or a modified sorption equilibrium isotherm must be used. From experience with the equation small values of K represent adsorption on a non-porous solid as will be shown later. It is improbable that experimental error is the cause of the negative value for K. Consequently the second possibility seems more probable.

In the derivation of the sorption equilibrium isotherm where K is the equilibrium constant of the reaction, $H_2O(\text{surface}) + D \rightleftharpoons D \cdot H_2O$, it was assumed that the effective concentrations to be used were Σ , $(1 - \phi)$, and ϕ for adsorbed water, empty interior sites (D), and filled interior sites ($D \cdot H_2O$) respectively. These formulations for D and $D \cdot H_2O$ are equivalent to the assumption that the number of sites is independent of the amount of adsorption as found experimentally for the sorption of methanol by cellulose. If the Pauling suggestion is adopted that the number of interior sites per gram increases as sorption increases then the effective concentration of unoccupied sites should be given by $1 - \phi + f(\phi)$. The nature of $f(\phi)$ is unknown but if $f(\phi)$ is expressed as $\alpha\phi$ where α is an adjustable parameter then the resulting values of K for salmin are positive and the equation for the sorption equilibrium isotherm becomes,

$$W_e = \frac{AK\Sigma}{1 + K\Sigma(1 - \alpha)}$$

To date only one example, that of salmin, has been found where K is negative with $\alpha = 0$ and until other examples are found it seems unnecessary to introduce the additional parameter,

The values of A, which is moles of interior (D) sites per gram of solid show a small decrease with increase in temperature. Excluding salmin the maximum change in A for a 15 degree temperature interval is of the order of 20%. The average change in A is about half of this. It would be anticipated that A would be independent of temperature or change slightly with the temperature.

In discussing Bull's results, Pauling (4) correlated the number of water molecules held in the first layer as calculated from the BET equation with the number of polar side groups present in the protein chain and found approximately a one to one correspondence. Taking Pauling's values for the moles of polar side groups per gram of protein and dividing these values into the previously listed values for A, ratios are obtained ranging from 3 to 5. These ratios are interpreted as meaning that each polar side group introduces sufficient disorder into a protein lattice that 3 to 5 water molecules are held in these disordered regions. With this modification the mechanism of the sorption of polar molecules by proteins as deduced from the new isotherm is essentially identical with the concepts of Bull and Pauling.

Sorption of Polar Molecules by Nylon

Nylon is a condensation polymer of the polypeptide type with no polar side groups. In Table III are listed the values of A, K, and K_1 calculated for the sorption of various polar vapors on Nylon 66.

Table III
Sorption of Polar Vapors on Nylon 66

Ref.	Vapor	State	T	K_1 (atm. ⁻¹)	K	A (moles sites/gram)
3	H ₂ O	Unstretched	25°C.	105.42	0.2184	0.00688
3	"	"	40	27.63	0.3336	0.00551
3	"	Stretched	25	95.56	0.3717	0.00473
3	"	"	40	31.24	0.4235	0.00417
5	"	?	40	32.65	0.1825	0.00754
5	CH ₃ OH	"	25	12.66	0.1128	0.01412
5	C ₂ H ₅ OH	"	25	22.96	0.2240	0.00695
5	C ₂ H ₅ CN	"	25	30.15	0.2797	0.00116

5. J. A. Cutler and A. D. McLaren, *Tappi*, **36**, 423 (1953)

For the results in Table III it will be noted that the sorption of water by nylon is much less than the sorption of water by proteins as indicated by the lower values for A. The lower values for A for nylon indicate as is known from other evidence that nylon has a high degree of order or a low degree of disorder. Part of the disorder in nylon must arise from the fact that the chain length of the nylon polymer is much smaller than that in natural polymers. Each chain end can be considered as a disturbance center in the vicinity of which disorder must occur. The molecular weights of the particular nylon samples are not known but if the chains have an average molecular weight of 10,000 then the number of disturbance centers would be 2×10^{-4} centers per gram of nylon. From the protein data it appears that each polar side group or one disturbance center furnishes sorption sites for 5 molecules of water. If we use the same assumption, the value of A for nylon would be 1×10^{-3} sites per gram in comparison with the experimental value of 4 to 5×10^{-3} sites per gram. Exact agreement would require an average molecular weight for nylon of 2,000 to 2,500.

In the disordered regions complete hydrogen bonding between adjacent chains has not taken place. Sorption is probably limited to such regions as it is unlikely that molecules of any vapor can permeate any region having high order. As shown from the data in Table III, stretched nylon has lower disorder than the unstretched material.

It is interesting to note that the values of A vary with the nature of the vapor undergoing sorption. The value of A decreases in going down the series; CH₃OH, C₂H₅OH, and C₂H₅CN. This change in A is probably caused by the increase in molecular size in going from CH₃OH to C₂H₅CN. In other words all types of disordered regions are present ranging from those which can only be permeated by CH₃OH to those sufficiently disarranged to accommodate all polar molecules whose size is equal to or less than that of the C₂H₅CN molecule. Although H₂O as a small molecule would be expected to permeate as many disordered regions as any other molecule nevertheless the A values indicate that it is not as good as CH₃OH but is better than C₂H₅OH. The reason for this discrepancy is not known but it may involve the fact that the H₂O molecule can be considered multifunctional with respect to hydrogen bonding if the spacial configuration is just right.

Sorption of Methanol on Various Polymers

The sorption of methanol on coal and other natural polymers has been under investigation in this laboratory for several years. These data fit the sorption equilibrium isotherm. The values of A, K, and K_1 are tabulated in Table IV.

Table IV
Sorption of Methanol on Natural Polymers

Ref.	Solid	T	K_1 (atm. ⁻¹)	K	A (moles sites/gram)
2	Cotton linters	30°C.	14.51	0.7472	0.00261
"	" "	35	13.60	0.6505	0.00265
"	" "	45	9.91	0.5844	0.00264
6	Kincaid Lignite	45	44.13	0.5229	0.09444
"	Wyoming Coal	45	16.04	0.9037	0.00648
1	Pittsburgh Coal	30	21.61	1.8941	0.00170
1	" "	35	29.55	1.1859	0.00172
1	" "	40	32.00	1.1700	0.00180

6. P. Fugassi and G. Ostapchenko, unpublished

The solids in Table IV have been listed in order of decreasing oxygen content. Cellulose is considered a precursor of coal and if cellulose is considered as the lowest rank coal having zero geologic age, then the solids are listed in order of increasing rank. It will be noted that A has at first a low value, rises to a high value and then decreases. The low value of A for cellulose is due to high order being present. With increasing age and rank order is destroyed and simultaneously oxygen content decreases. The low values of A for Pittsburgh Seam coal is not due to order but arises from the small amount of oxygen containing gel present in the coal. For Pittsburgh Seam coal the values of K_1 increase as temperature increases. This is the only system for which this behavior has been found.

Other Systems

Data are in the literature for a wide variety of possible combinations such as polar and non-polar gases on non-porous solids, polar compounds on porous, inelastic wall gels, etc. The sorption equilibrium isotherm has been applied to such systems although the properties of these systems are not in agreement with those assumed for the derivation of the equation. It is found that the experimental data can be fitted to relative pressures of 0.9. A tabulation of these data are given in Table V.

Table V
Values of Parameters for Various Systems

Ref.	Adsorbent	Adsorbate	T	K_1 (atm. ⁻¹)	K	A (moles sites/gram)
7	Charcoal	n-caproic acid-H ₂ O	25°C.	266.1	0.3439	0.00112
"	"	n-amyl alcohol-H ₂ O	"	68.8	0.5221	0.00093
"	"	phenol-H ₂ O	"	27.3	0.7416	0.00112
8	Ag	n-C ₄ H ₁₀	-78°	336.6	0.0282	0.00034
"	"	CHCl ₂ F	"	1398.5	0.0161	0.00052

7. R. S. Hanson, Y. Fu, and F. E. Bartell, J. Phy. Chem., 53, 769 (1949)
8. R. T. Davis, Jr.; T. W. DeWitt, P. H. Emmett, J. Phy. Chem., 51, 1232 (1947)

For such systems the equation must be considered as empirical. Ag is a non-porous solid and has a low value for A. Increased polarity of the gas increases K_1 (n C₄H₁₀ relative to CHCl₂F). While the sorption equilibrium isotherm

must be considered as empirical for these systems, it is possible that such an equation might be valid for non-porous solids if the surface is heterogeneous and composed of two types of sites having properties similar to the S and D sites postulated for elastic wall gels.