Reports

Electrostatic Aspects of Physical Adsorption: Implications for Molecular Sieves and Gaseous Anesthesia

Abstract. *The equations of electrostatics are applied to the adsorption of gases on molecular sieves; separations on sieves are caused not by the size of molecules but by electrostatic forces between the gases and the strong electric fields of the sieves. Electrostatic interactions can also explain the phenomenon of general anesthesia.*

The relation of electrostatic forces to physical adsorption was initially used by DeBoer and Zwicker (*1*) to explain multilayer adsorption on solids. They assumed that the surface ions of the adsorbent induced dipoles in the first layer of adsorbed molecules; and the dipoles in turn induced other dipoles in the next layer and so on until several layers were built up. Bradley (*2*) used the theory of DeBoer and Zwicker to explain the adsorption of argon on dehydrated aluminum and cupric sulfates. Later, this polarization theory of multilayer adsorption was criticized by Brunauer, Emmett, and Teller (*3*) who showed that the polarization of one layer of adsorbed molecules by the next lower layer was too small to constitute the major portion of the binding energy between successive adsorbed layers. Because of this criticism the polarization theory of multilayer adsorption was abandoned, probably prematurely.

Since the work of Brunauer, Emmett, and Teller most investigators have entirely neglected, or have given only cursory treatment to, electrostatic forces in physical adsorption. However, Benson, and co-workers (*4*) successfully utilized electrostatic interactions to explain the sorption of gases on finely divided, crystalline proteins. It now appears that electrostatic interactions are important for many of the adsorbents used in physical adsorption studies, especially the most popular of the adsorbents, γ-Al_2O_3. King and Benson (*5*) have shown, in explaining the low temperature adsorption of the hydrogen isotopes on γ-Al_2O_3, that the adsorbent has very strong surface electric fields. They calculated the electric fields over the (100) plane of an Al_2O_3 surface and found two types of sites with very strong electric fields and several types with much weaker fields. These fields arise primarily from normal structural vacancies in the crystal lattices and all "defect" structures, such as 1-2, 3-2, or 3-4 lattices, must have these vacancies in order to maintain charge neutrality. The MgO and NaCl lattices have only very weak surface fields.

Since many such "defect" structures are used as adsorbents, the attractive forces between the gas and solid may be electrostatic. For gases with no permanent dipole, the induced-dipole attractive potential is

$$\Phi_i = -\frac{\alpha_i}{2} E_z^2 \qquad (1)$$

where α_i is the principal moment of polarizability of the adsorbed molecule and E_z, the electric field intensity normal to the surface. E_z usually falls off very rapidly with the distance from the surface.

For gases with permanent dipole moments, an additional and usually larger ion-dipole attraction exists:

$$\Phi_p = \mu E_z \qquad (2)$$

where μ is the dipole moment of the gas.

Equations 1 and 2 explain much of the experimental data of physical adsorption. King and Benson (*5*) successfully used Eq. 1 to explain the low-temperature chromatographic separation of the hydrogen isotopes and Eq. 2 to explain the adsorption of a polar material, like water, on Al_2O_3. They concluded that graphite, on which Sandler (*6*) separated *o*- and *p*-hydrogen, must have an ionic surface layer. This would account for the fact that water forms a monolayer on graphite.

We now report that electrostatic interactions are dominant in other physical-adsorption systems. We shall present evidence that electrostatic interactions play a prominent role in the physical adsorption of gases on so-called "molecular sieves" and may also be important in biochemical processes in that they suggest a new interpretation of the mechanism of general anesthesia in the brain.

Strong experimental evidence that electrostatic forces are involved in physical adsorption on molecular sieves is the fact that *o*- and *p*-hydrogen can be separated on these materials. Bachmann, Bechtold, and Cremer (*7*) chromatographically separated *o*- and *p*-hydrogen on the Linde synthetic molecular sieves 5A and 13A. Their separation factor, defined as the ratio of the corrected elution times, was 1.40, which is approximately equal to that found on γ-Al_2O_3 surfaces (*8*). In order for the *o*- and *p*- species to be separated there must be some type of hindered rotation of the adsorbed molecules since these species differ only in rotational energy. A barrier height of approximately 0.8 kcal/mole is needed to produce a separation factor of 1.40 for *o*- and *p*-hydrogen (*5*). It is improbable that any type of van der Waals interaction could account for such a large barrier. However, strong electrostatic forces can produce very large barriers to rotation. King and Benson, using Eq. 1, showed that the known difference in the parallel and perpendicular components of the polarizability of hydrogen can account for the necessary barrier height on a γ-Al_2O_3 surface. Since the experimental separation factors are comparable, the evidence suggests that molecular sieves also have strong electric fields which polarize and attract molecules to the surface. From the fact that the parallel component is about 30 percent larger than the perpendicular component we conclude that the H_2 molecule is held with its axis perpendicular to the surface of the solid absorbent.

The existence of strong electric fields in molecular sieves is suggested by the fact that the separation of nonpolar gases on a chromatographic column packed with a molecular sieve is a monotonic function of the gas polarizability. The relative retention volumes of several gases on a molecular-sieve column (*9*) are shown as a function of their polarizabilities (Fig. 1).

From the theory (*5*) we would expect such a curve to be very close to a straight line. The large deviations from the straight line, notably those of N_2 and C_2H_6, can be attributed to the sizes of the molecules, since the interactions are also functions of the equilibrium distance of the molecules from the surface. In fact, the expression for the field in Eq. 1 can be replaced by $e_{\text{eff}}^2/(r\text{-}r_0)^4$ where e_{eff} is an effective charge, r is the distance between the adsorbed molecule and the surface, and r_0 is the radius of the adsorbed molecule. Since the data in Fig. 1 shows a maximum of 30 percent and an average deviation of only 7 percent from the line drawn, this is a rather striking confirmation of the theory. Further support for the theory comes from the fact that such pairs as neon and hydrogen, oxygen and nitrogen, and methane and krypton show only slight deviations from the line. These pairs have long been considered somewhat mysterious anomalies (*10*).

We can ascertain the origin of the electric fields by examining the structure of the sieves. The sieves are actually crystalline aluminosilicates, also known as zeolites. Many of the zeolites are naturally occurring minerals whose structures are very similar to those synthesized by Linde. Their general composition is always of the type $[M_x/n][(AlO_2)_x(SiO_2)_y]\ z\ H_2O$, where n is the charge on the metal cation, M^{n+} (usually Na^+, K^+, or Ca^{2+}), and z is the number of moles of water of hydration, which is highly variable. Their structure is composed of a complex arrangement of SiO_4 and AlO_4 tetrahedra, linked by the cation in such a manner that an open structure with wide channels is created. The water of hydration is located within these channels, but it can easily be driven off by heating which activates the zeolites for chromatographic columns.

The structure of one of the naturally occurring representative zeolites, analcite (Fig. 2), was determined by Taylor (*11*); in Fig. 2 the small spheres represent sodium ions and the large spheres water molecules.

During the activation process when the water molecules are driven off, the channels are occupied only by the cations which, because of their uncompensated charge, produce very strong electric fields. The ions also serve as adsorption sites because of the strong electrostatic attractive energy between an ion and a polar or nonpolar molecule. For the polar molecule:

$$\Phi_p = -\frac{C_{A+}\mu_p}{r^2} \qquad (3)$$

where C_{A+} is the charge on the cation, μ_p the dipole moment of the polar molecule, and r is the interaction distance.

For nonpolar molecules,

$$\Phi_{np} = -\frac{\alpha\, C_{A+}^2}{2r^4} \qquad (4)$$

which is similar to Eq. 1.

The attractive energy of the water of hydration, originally present at these sites, is given by Eq. 3. Like Eq. 1, Eq. 4 also leads to the type of curve shown in Fig. 1 for nonpolar molecules.

The existence of the open channels in the zeolite structure has led Barrer (*12*), as well as others, to postulate that the adsorption and separation of gases is determined primarily by the comparative size of the molecules and the channels. This belief caused McBain (*13*) to call the zeolites "molecular sieves." However, the fact that molecules, such as O_2 and N_2, which are small enough to fit into the channels are also separated by the "sieves" was never explained.

The electrostatic model suggests that the separation of gases on molecular sieves is governed by Eqs. 1–4 and not by comparative sizes. The fact that some large molecules are not adsorbed on molecular sieves could be attributed to their bulkiness, which prevents them from interacting strongly with the adsorption sites on the sieves.

Another observation in support of the electrostatic hypothesis is that the adsorption properties of the zeolites change on replacement of the original cation in the channel with a cation of different charge (*14*). We must, therefore, conclude that the physical adsorption and separation of gases on molecular sieves are not primarily due to the caging of molecules but are caused by electrostatic interactions of the molecules with the local electric fields of the cations present in the structure. In fact, there is little or no direct experimental evidence to suggest that it is any but the "external" surface area which is effective in adsorption by the "sieves" (*15*).

In many of the theories of anesthesia the most important properties of the anesthetizing agent appear to be the polarizability and the molecular size. In the Overton-Meyer lipid solubility theory (*16*), which states that gases possessing narcotic action are adsorbed preferentially by cells with high lipid content, the magnitude of the lipid solubility is a measure of the attraction between the gas and lipid molecule and can be correlated with the polarizability and size of the gas molecule. This theory, however, does not explain the mode of action of the drug in the cell; it only explains the transport of anesthetic drugs to and into the cells.

Of the theories which attempt to explain the mechanism of anesthesia, the hydrate theories of Pauling (*17*) and Miller (*18*) are the best known. Pauling states that . . . . "general anesthetics of the nonhydrogen bonding type such as cyclopropane, chloroform, nitrous oxide, and 1,1,1-trifluoro-2-chloro-2-bromoethane(halothane), operate by increasing the impedance of the encephalonic network of conductors, and that this increase in impedance results from the formation in the network, presumably mainly in the synaptic regions, of hydrate microcrystals formed by crystallization of the encephalonic fluid. These hydrate microcrystals trap some of the electrically charged sidechain groups of proteins and some of the ions of the encephalonic fluid, interfering with their freedom of motion and with their contribution to the electric oscillations in such a way as to increase the impedance offered by the network to the electric waves and thus cause the level of electric activity of the brain to be restricted to that characteristic of anesthesia and unconsciousness, despite the continued activity of the exciting mechanism."

Pauling supports his hypothesis by correlating both the partial pressure of anesthetic agents in equilibrium with their hydrate crystals and ordinary ice and water at 0°C and the anesthetizing partial pressure for mice with the molar refraction of the anesthetic agents (see *19*).

Miller also considered the possible role of hydrates in anesthesia. He found a correlation between the dissociation pressure of gaseous hydrates at 0°C and anesthetic potency, but he estimated that 34 times the pressure needed at 0°C is necessary for the existence of the hydrates of the smaller gases at body temperature (37°C) and 1000 times the pressure for the larger gases.

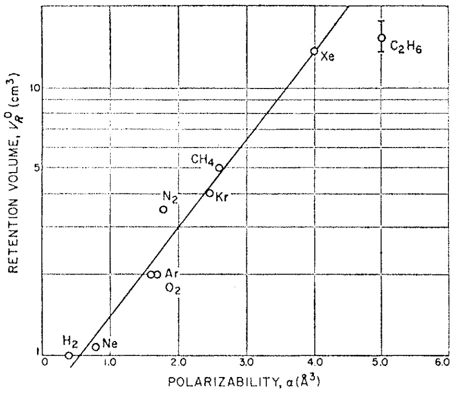

Fig. 1. The relative retention volumes on a Linde 5A molecular sieve column at 100°C as a function of the molecular polarizabilities.

Because of this and the fact that several of the gases would at 37°C liquefy, Miller concluded that it is doubtful that crystalline hydrates could form during anesthesia even if they are stabilized by protein side chains as suggested by Pauling. As an alternative Miller proposed the formation of "icebergs" or "ice covers" which he described as being formed when gas molecules orient water around themselves, much as proteins do, so that the molecules are surrounded by a shell of water which is in a more highly ordered state than is the remainder of the water. The support for this type of "iceberg" comes from the fact that liquid water has some type of ice-like structure—which may or may not be like the structures of the hydrates—except that "free" water molecules occupy the center of the cages (*20*). Miller also showed a correlation between the partial pressure for anesthesia and that portion of a hypothetical surface covered with structured water (ice cover) in the different stages of anesthesia. Miller contends that his "icebergs" differ from Pauling's microcrystals in being much smaller and not crystals in the usual sense.

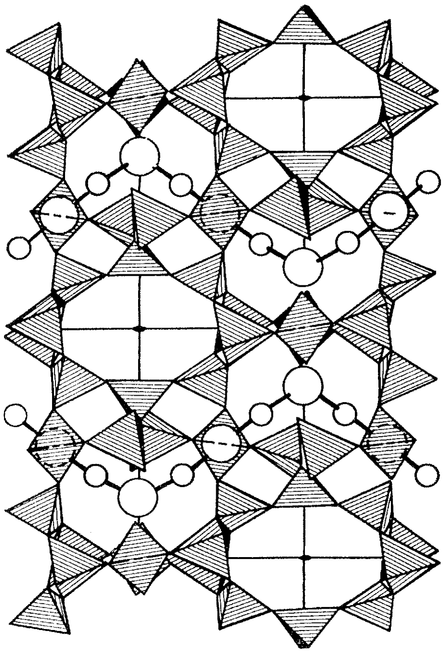

Fig. 2. Structure of analcite, projected into the (100) plane; chains of the $[(Si, Al)_{12}\ O_{24}]$ group are arranged parallel to the *c*-axis. Small spheres represent sodium ions and large spheres represent water molecules.

However, the two theories suffer from two deficiencies. One of these is the lack of stability of the "hydrates" at 37°C. It is rather doubtful that either the "icebergs" or Pauling's microcrystals are stable at body temperature. A somewhat more serious drawback to the theories is the fact that many gases with anesthetic properties do not form hydrates. The most notable of these is diethyl ether, but the list also includes hydrocarbons higher than propane, aromatic hydrocarbons, various ethers, and halogenated derivatives of these compounds. Also, there are a number of gases, such as H_2S, SO_2, Cl_2, O_2, $CHCl_2F$, C_2H_5F, and others, which form hydrates but are not known to have anesthetic properties. In all cases, these gases elicit acute toxic reactions at pressures lower than those necessary for narcosis.

If instead of hydrate formation, the gases interact directly with some charged sites on the nonaqueous phase (*21*), the interaction would be a function of the polarizabilities of the gases in accordance with Eq. 4. While Pauling used the very striking correlation between the partial pressure necessary to anesthetize and the molar refraction to support his suggestions of "hydrate" formation, this correlation provides equally strong support for an "adsorptive" model in which the adsorptive forces are primarily electrostatic. Whatever the detailed mechanism of nerve conduction may be, any model must evolve from considerations of the surface potentials at the interface between an essentially organic, nonconducting, lipid, cell wall and an aqueous, electrolytic solution. Our electrostatic model suggests that polarizable molecules such as argon or cyclopropane which are dissolved in the aqueous phase will tend to be preferentially adsorbed at charged sites on the organic phase and that this sorption will follow the polarizabilities in much the same way that it does on the sieves. Such reversible sorption would be expected to alter the surface potentials and impede the conduction of charges across the interfaces thereby providing a pathway for anesthetic action.

The electrostatic theory does not suffer from the deficiencies of the "hydrate" theories. The molecules which do not form hydrates but are anesthetic agents are not excluded. The fact that dimethyl ether falls along Pauling's curve of anesthetizing pressure plotted against molar refraction supports the inclusion of the nonhydrate-forming gases. Also, it is not surprising that helium, hydrogen, and probably neon have no anesthetic effect (*18*) since these gases have the lowest polarizability values. Size must be also considered in the electrostatic model, but it does not prevent hydrocarbons with more carbon atoms than propane, aromatic hydrocarbons, and various others from being anesthetic agents even though they do not form hydrates.

While Miller's and Pauling's theories both relate the anesthetic reaction to an immobilization of fluid water and both implicate (although for different reasons) charged sites on surfaces, neither examines critically the problem of why such charged sites would react with the anesthetic molecule or how the charged site is related to a nerve conduction. The minor changes in bulk electrical conductivity in the cerebral fluid, which the extremely small mole fractions of dissolved agents would produce, seems hardly likely to be significantly related to nerve conduction. The specific site adsorption suggested by the electrostatic viewpoint is a much more reasonable mechanism for the blocking of nerve conduction.

Whereas it is not too difficult to make a detailed model and a calculation of gas adsorption on a solid substrate (*5*), it is much more difficult to do so for partition between an aqueous solution and a wetted surface. One must consider the free energy change in the process of agent A going from aqueous phase to wetted surface site S with displacement of water:

$$A(aq) + S(aq) \rightleftharpoons S \cdot A(aq) + \text{free water} \qquad (5)$$

For these reasons we have not attempted a general calculation of the equilibrium constant for such a process, and the direct application of Eqs. 4 and 3 can be misleading.

That sorption of anesthetics at aqueous interfaces is large and important at the partial pressures effective in anesthesia has been demonstrated by the measurements of Clements and Wilson (*22*).

Since all of the accepted theories of gaseous anesthetics involve in some way molecular polarizabilities and molecular sizes, the electrostatic "adsorption" theory simplifies the situation by eliminating the necessity of "hydrate" or other aggregate formations.

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14 September 1965

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Clathrate Structure of Silicon Na_8Si_{46} and Na_xSi_{136} ($x < 11$)

Abstract. *The crystal structure of two new cubic phases in the silicon-sodium system have been solved from their x-ray diffraction patterns. Both structures are of the clathrate type found for gas hydrates, consisting of tetrahedral networks which are combinations of pentagonal dodecahedra with 14-face polyhedra in one case and with 16-face polyhedra in the other case. There is strict correspondence between the silicon positions and the oxygen positions of the hydrate structures. For one compound,* Na_8Si_{46}, *the centers of all polyhedra are occupied by sodium atoms. For the other compound, there occurs only partial occupancy of the polyhedral cages.*

Two new phases (*1*) in the silicon-sodium system have recently been prepared, isolated, and characterized by means of chemical analysis, density, and Debye-Scherrer x-ray diffraction patterns. One of the phases could be described quite well by the formula $NaSi_6$ and a simple cubic unit cell with a equal to 10.1 ± 0.02 Å containing eight formula weights. The other phase was nonstoichiometric and corresponded to the formula Na_xSi with $0.02 < x < 0.08$. This phase, too, is cubic with a equal to 14.62 ± 0.02 Å but of higher symmetry with the space group *Fd*3*m*. The lattice parameter (but not the intensity of a given reflection) was independent of the sodium content. The number of silicon atoms per unit cell was reported to be 132.

We now report that we have deduced the crystal structures of both phases from the diffraction patterns and the other information reported by Cros *et al.* (*1*). Both structures are of the clathrate type found for gas hydrates (*2–4*) in which there are tetrahedral networks of oxygen positions occurring as pentagonal dodecahedra combined with 14-face polyhedra in one case and 16-face polyhedra in the other. The two silicon structures correspond to the two most common examples of gas hydrate structures for which the respective numbers of atoms per unit cell in the tetrahedral network are 46 and 136. The sodium atoms occur in the centers of the polyhedral cages just as the "guest" molecules do in the hydrate structures.

For Na_8Si_{46}

Cubic, $a = 10.19 \pm 0.02$ Å
Space group *Pm*3*n*
6 Si_1 in 6(*c*) ¼o½
16 Si_2 in 16(*i*) xxx, $x = 0.183$
24 Si_3 in 24(*k*) oyz, $y = 0.310$, $z = 0.116$
2 Na_1 in 2(*a*) ooo
6 Na_2 in 6(*d*) ¼½o
Calculated density = 2.316 g/cm^3
Observed density = 2.27 g/cm^3

This structure is the analog of the hydrate structures $46\ H_2O \cdot 8M$. The most precise and detailed account of this structure type (*2*) is for the case where M equals Cl_2. Accordingly, we have used the parameters given for chlorine hydrate, which are the values that produce essentially equal Si—Si distances. We have assumed also that all the centers of silicon cages are filled with sodium to give close agreement with the reported silicon-to-sodium ratio (46/8 = 5¾, ∼ 6).

The intensities calculated for the proposed structure are given in Table 1 along with the observed values reported (*1*). Only Lorentz-polarization corrections, multiplicity factors, and a normalization factor have been applied to the calculated F^2 values which include a temperature factor with $B = 1$ Å^2. The excellent agreement for intensities (Table 1) substantiates the correctness of the assumed model and indicates little if any need for refinement of structural parameters.

Each silicon atom forms four bonds of 2.37 Å to other silicon atoms in a distorted tetrahedral arrangement. The bond distance in ordinary silicon is 2.35 Å. The sodium atom in the smaller cage (Na_1) is 3.23 Å from eight of the silicons and 3.37 Å from 12 others. In the larger cage Na_2 is 3.41 Å from 12 silicons, 3.79 Å from eight others, and 3.60 Å from four others. The sodium-silicon distances are all much too large for any appreciable direct bonding by sodium atoms. It would appear then that the Na atoms are essentially uncharged.

For Na_xSi_{136}

Cubic, $a = 14.62 \pm 0.02$ Å
Space group *Fd*3*m*
Atomic positions: (ooo, ½½o, ½o½, o½½) +
8 Si_1 in (*a*) ooo, ¼¼¼
32 Si_2 in (*e*) xxx; $x = -0.094$
96 Si_2 in (*g*) xxz, $x = -0.058$, $z = -0.246$
8α Na_1 in (*b*) ½½½, ¾¾¾
16β Na_2 in (*c*) ⅛⅛⅛