ADSORPTION POTENTIAL NEAR SPHERICAL PARTICLES OF COLLOIDAL DIMENSIONS

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Abstract

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ADSORPTION POTENTIAL NEAR SPHERICAL PARTICLES OF COLLOIDAL DIMENSIONS

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Disperse systems consisting of very small particles of spherical shape attract the interest of researchers, since among these systems there are practically important objects—for example, carbon blacks, silica gels, titanium gels, etc.—which, according to electron microscopy data, possess a globular structure, and the particle sizes can often easily be determined with sufficient accuracy. In addition, in studying these systems, certain fundamental questions of adsorption theory can be clarified, since the simple geometry facilitates the necessary calculations without invoking any hypotheses about the structure of the system. On the basis of general ideas about an increase of the adsorption potential in slits, pores, and cracks of a sorbent, considerations are sometimes expressed about an increase of the potential near the point of contact of spherical particles. Therefore one might suppose that, for some sorbents composed of nonporous spherical particles, such an increase in potential should be reflected in the form of the vapor adsorption isotherm. However, this proposition requires quantitative verification, which has not yet been carried out even in a first approximation.

Let us first consider the adsorption field created near an isolated (single) spherical particle of diameter $\delta = 2r$ at a distance d from its surface. It is most expedient to carry out this calculation by comparing the adsorption potential P of the particle with its value at the same distance for a flat surface, where it is equal to P_∞. It may be asserted *a priori* that $P < P_\infty$, with the decrease in potential being due to the action of two causes: the influence of the surface curvature and the finite dimensions of the particle. The calculation proposed by us applies to particles whose diameters lie in the interval 100–2000 Å, which corresponds to the sizes most often encountered among silica gels, carbon blacks, etc. To estimate the possibility of formation of polymolecular layers, the value of the potential was calculated at distances from the surface amounting to 3–7 radii of the adsorbate molecules. Under these conditions the distance d exceeds several times the distance between adsorbent molecules, and in calculating the adsorption potential, integration may be used instead of summation without appreciable error.

The volume element of the adsorbing particle, as the differential of the volume of a spherical segment, is equal to

$$dv = \pi R \left(2R - r - d + \frac{r^2 - R^2}{r + d} \right) dR.$$

Therefore the adsorption potential at a point lying at a distance d from the surface is expressed as

$$P = \pi N \int_d^{2r+d} f(R) R \left(2R - r - d + \frac{r^2 - R^2}{r + d} \right) dR, \tag{1}$$

where $f(R)$ is the interaction potential of an adsorbent molecule with an adsorbate molecule. Without entering into a discussion of the nature of this interaction, one may, in any case, represent this function in the general form [1]:

$$U = f(R) = -\left(\frac{B}{R^6} + \frac{C}{R^8} \right) + De^{-R/\rho} \tag{2}$$

or

$$f(R) = f_1 + f_2 + f_3.$$

Here the first two terms characterize attraction, and the last one repulsion. For a plane surface, as is known [2]:

$$P_\infty = 2\pi N \int_d^\infty f(R)\, R(R - d)\, dR.$$

Hence, applying expression (2), we find

$$P_\infty = P'_\infty + P''_\infty + P'''_\infty,$$

where

$$P'_\infty = -\frac{1}{6}\pi B N d^{-3}; \qquad P''_\infty = -\frac{1}{15}\pi C N d^{-5}; \qquad P'''_\infty = 2\pi D N \rho^3 e^{-x}(2 + x)$$

and $x = d/\rho$. For a spherical particle, substitution of the corresponding values from (2) into formula (1) and integration lead to other relations, which after reduction take the form

$$P = \alpha P'_\infty + \beta P''_\infty + \gamma P'''_\infty,$$

where

$$\alpha = (1+\eta)^{-3}; \qquad \beta = \frac{2.5\eta^2 + 2.5\eta + 1}{(1+\eta)^5};$$

$$\gamma = \frac{e^{-y}(y^2 + \eta y^2 + 2\eta y + 4y + 6) - (2\eta y - \eta y^2 - 2y + 6)}{y(2\eta + 1)(2 + \eta y)}.$$

Here $\eta = d/\delta$ and $y = \delta/\rho$ have been put. In the last formula, owing to the large values of y (for example, at $\rho = 0.2$–0.5 Å the value of y is 300–2000), the first term in the numerator is negligibly small, and may be neglected. Then

$$\gamma = (2\eta + 1)^{-1}\left[1 - \frac{2(\eta y + 3)}{y(\eta y + 2)}\right]$$

or, for $y \simeq 10^3$, more simply:

$$\gamma \simeq (2\eta + 1)^{-1}.$$

Therefore, finally:

$$P = (1+\eta)^{-3} P'_\infty + \frac{2.5\eta^2 + 2.5\eta + 1}{(1+\eta)^5} P''_\infty + (2\eta + 1)^{-1} P'''_\infty.$$

It is easy to see that all the quantities α, β, and γ are always not greater than unity, and that they attain their maximum value at $2r \to \infty$, or $\eta \to 0$, i.e., above a plane surface. Hence it follows that

$$P < P_\infty.$$

Table 1 gives the values of the coefficients α, β, and γ for different η, found from the formulas.

These results show that, in the range of the indicated particle sizes and distances d, when the values of η lie in the interval from 0.005 to 0.10, the coefficients α, β, and γ differ appreciably from unity, corresponding to a plane surface. However, apparently, the contributions of the quadrupole term

the repulsion components are small in comparison with the contribution of the dipole term, and they may be neglected. But, in any case, it may be expected that above a single particle at distances of 2-3 molecular layers one should take into account a lowering of the adsorption potential by 10-20% in comparison with the value above a plane surface at the same distance.

Passing to contacting particles and confining ourselves, for simplicity, to particles of equal size, let us note that near such systems the potentials from the individual particles are added additively. Thus, for a pair of contacting particles, at points lying on the common tangent and equidistant from both particles, the potential is simply doubled. Consequently, here we have:

$$P_{1,2} = 2P = 2(\alpha P'_\infty + \beta P''_\infty + \gamma P'''_\infty).$$

Table 1

η	α	β	γ, $y = 100$	γ, $y = 1000$
0	1	1	1	1
0.005	0.985	0.990	0.962	0.987
0.01	0.971	0.975	0.953	0.978
0.02	0.942	0.953	0.938	0.959
0.05	0.864	0.888	0.888	0.908
0.10	0.751	0.792	0.814	0.831
0.30	0.455	0.532	0.612	0.624
0.50	0.296	0.377	0.490	0.500
1.00	0.125	0.188	0.327	0.333

For large particles with diameters of about 1000 Å and more, it is permissible to take $P_{1,2} = 2P_\infty$, since in this case $\alpha = \beta = \gamma = 1$. This corresponds to the maximum increase of the adsorption potential in the gap between two particles. Analogous calculations by de Boer and Custers (^{3}), and also by Melvin-Hughes (^{4}), for a concave hemisphere at its center gave $P = 4P_\infty$. In the case of a cylindrical well with a hemisphere at the bottom, one obtains at its center $P \simeq 6P_\infty$, and with all-round enclosure we have $P = 8P_\infty$. Therefore it may be said that in the gap between contacting particles the increase of the potential is relatively small even for the largest colloidal particles and becomes still smaller when the particles are small; for example, for the smallest of them one obtains $P_{1,2} \simeq 1.5P_\infty$.

In the formation of a group of 3 particles according to the closest-packing scheme, at the center, which is at a distance $\eta = 0.106$ from each particle, the adsorption potential is equal to $P_{1,2,3} = 3P$, or, for small particles, $P_{1,2,3} \simeq 3 \cdot 0.75P'_\infty \simeq 2.25P_\infty$.

In experimental studies one always has to deal with a large number of spherical particles. For loosely packed systems, on the basis of the preceding calculations one may expect a slight increase of the potential at the few contacts, which will be practically compensated by the lowering of the potential above the free surface of the particles, and therefore the adsorption isotherm should correspond closely to the isotherm for noncontacting particles, other conditions being equal.

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CITED LITERATURE

1. R. Fowler, E. Guggenheim, *Statistical Thermodynamics*, IL, 1949, p. 346.
2. F. London, *Zs. Phys. Chem.*, (B), **11**, 222 (1930).
3. J. H. de Boer, J. F. H. Custers, *Zs. Phys. Chem.*, (B), **25**, 225 (1934).
4. E. A. Moelwyn-Hughes, *J. Coll. Sci.*, **11**, No. 4–5, 501 (1956).

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