PHYSICAL BASIS UNDERLYING THE THEORY OF POLYMOLECULAR ADSORPTION FILMS AND OF CAPILLARY CONDENSATION OF POLAR LIQUIDS.

II. DETERMINING THE ADSORPTION POTENTIAL OF A MODEL WHICH APPROXIMATES THE STRUCTURE OF FINE DISPERSIONS

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An analysis is made of the conditions under which polar molecules are adsorbed at surfaces of finite dimensions. On the basis of the nonuniformity of the electric-field topography of an adsorbent surface, an expression is derived for the adsorption potential and suitable for thermodynamic calculations of surface phenomena.

The adsorption potential φ will be defined as the work of adsorption forces in moving an adsorbate molecule from infinity to the interface between adsorption film and adsorbate vapor. This work is numerically equal to the excess potential energy $\Pi - \Pi_\infty$ of the given molecule in the adsorbent field, but has the opposite sign.

A quantitative determination of φ is rather difficult and the problem has not yet been solved completely, mainly because the expressions for the potentials of molecular adsorbent–adsorbate and adsorbate–adsorbent interaction have not been completely developed while there are no test data available on the state of adsorbed molecules and their complexes [1]. Furthermore, the residual nonhomogeneity of a solid surface not only makes it difficult to calculate the adsorption potential of a given substance but also has a large effect on the repeatability of adsorption test data. For this reason, the determinations of the adsorption potential reported in the technical literature [2-5] apply mainly to models of pure substances with homogeneous surfaces.

Thus, the adsorption potential of polydisperse substances, which are considered in this study, can be calculated only approximately and the problem reduces to the correct choice of a model which will best represent the actual adsorbent. According to the test data in [6, 7] pertaining to surface properties of various substances (silica gel, wood pulp, cereals), at the surfaces of these substances there exist certain active groups (for example, dipolar H–O-radicals). The surface of such a sorbent resembles a dipole lattice. Since the electric-field topography of such a surface is nonuniform [8, 9], and also since it is geometrically not homogeneous (due to granules, notches, fractures, and inclusions), hence the lattice is of finite size and forms a systematic domain structure of pores and gaps. The problem of determining the adsorption potential of such a model can be reduced, approximately, to that of calculating the potential energy of interaction between a polar sorbate molecule and a finite surface of a dipole lattice in the sorbent, the latter carrying similarly oriented dipoles of hydroxyl groups.

In the light of the preceding discussion, the potential energy of an elastic sorbate dipole in the domain field consists of the electrostatic energy due to both dipole–dipole and inductive interaction as well as of the energy due to dispersive interaction.* If the potential energy outside the field is assumed equal to zero, then by definition

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*The forces of dipole-quadrupole and of quadrupole–quadrupole interaction as well as the forces of sorbent–sorbate repulsion are all disregarded here, inasmuch as in our case the thickness of a polymolecular adsorption film is much greater than the intermolecular distances.

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$$\varphi = -(\Pi - \Pi_\infty) = mE + 2\pi\varepsilon_0\alpha E^2 + \varphi_{\text{disp}}. \tag{1}$$

We will now examine the field intensity due to a single domain, as a function of the distance z from this domain, and a mere qualitative analysis of the problem will allow us to draw the following conclusions:

1. At sufficiently great distances z the field may be regarded as the field due to dipoles uniformly "spread" over a finite small area.

2. As z decreases, the magnitude of the field intensity becomes appreciably affected by the discreteness of the dipoles.

Evidently, a field due to a domain depends on the two said factors: the boundary effect and the discreteness of dipoles:

$$\bar{E}_0 = \bar{E}_{0r} + \bar{E}_{0g}. \tag{2}$$

The $\bar{E}_{0g}$ component of field intensity associates with the strong bond between a monolayer and the adsorbent surface, while the $\bar{E}_{0r}$ component (together with the dispersive component) associates with the far-range effect of intermolecular interaction forces during polymolecular adsorption.

In the general case $\bar{E}_0$ can be calculated as the sum of the field intensities due to all dipoles in the lattice [10]:

$$\bar{E}_0 = \frac{1}{4\pi\varepsilon_0} \sum \frac{m_r}{R^3} (\bar{r}_0 \cos\beta + \bar{\beta}_0 \sin\beta). \tag{3}$$

For the purpose of this analysis, however, it is preferable to derive a functional relation for $E_0(x, y, z)$. We, therefore, revert to formula (2) and consider both components separately. We find the field potential at any arbitrary point $M(x_0, y_0, z_0)$ due to a plane square domain whose side is 2a and whose area is covered by uniformly distributed charges with the surface density σ_r. The potential due to a single dipole is

$$\psi = \frac{m_r \cos\beta}{4\pi\varepsilon_0 R^2}. \tag{4}$$

Since $R^2 = z_0^2 + (x-x_0)^2 + (y-y_0)^2$ and $\cos\beta = z_0/R$, hence

$$\psi = \frac{m_r z_0}{4\pi\varepsilon_0 [z_0^2 + (x-x_0)^2 + (y-y_0)^2]^{3/2}}, \tag{5}$$

or in differential form

$$d\psi = \frac{\sigma_r z_0 dx dy}{4\pi\varepsilon_0 [z_0^2 + (x-x_0)^2 + (y-y_0)^2]^{3/2}}. \tag{6}$$

The field potential due to the entire area is

$$\psi_r = \frac{\sigma_r z_0}{4\pi\varepsilon_0} \iint\limits_{-a}^{a} \frac{dx dy}{[z_0^2 + (x-x_0)^2 + (y-y_0)^2]^{3/2}}. \tag{7}$$

An evaluation of the integral in (7) yields

$$\psi_r = \frac{\sigma_r}{4\pi\varepsilon_0} \left\{ \operatorname{arctg} \frac{(a+x_0)(a+y_0)}{z_0 [z_0^2 + (a+x_0)^2 + (a+y_0)^2]^{1/2}} + \operatorname{arctg} \frac{(a-x_0)(a-y_0)}{z_0 [z_0^2 + (a-x_0)^2 + (a-y_0)^2]^{1/2}} \right.$$
$$\left. + \operatorname{arctg} \frac{(a+x_0)(a-y_0)}{z_0 [z_0^2 + (a+x_0)^2 + (a-y_0)^2]^{1/2}} + \operatorname{arctg} \frac{(a-x_0)(a+y_0)}{z_0 [z_0^2 + (a-x_0)^2 + (a+y_0)^2]^{1/2}} \right\}. \tag{8}$$

With the aid of Eq. (8) we find the field intensity at the center point M(0, 0, z):

$$E_{0r} = -\operatorname{grad}\psi = \frac{2a^2\sigma_r}{(a^2+z^2)(2a^2+z^2)^{1/2}\pi\varepsilon_0}. \tag{9}$$

If the additional field due to the mirror image of the dipole lattice [10] is also taken into account, then we have

$$E_{0r} = \frac{2a^2\sigma_r}{\pi\varepsilon_0} \left\{ \frac{1}{(a^2+z^2)(2a^2+z^2)^{1/2}} + \frac{\varepsilon_r - 1}{\varepsilon_r + 1} \cdot \frac{1}{[a^2 + (z+L)^2][2a^2 + (z+L)^2]^{1/2}} \right\}. \tag{10}$$

Analogously we can derive the field potential and the field intensity due to a spherical domain (grain radius r, domain radius a):

$$\psi_r = \frac{\sigma_r}{2\varepsilon_0}\left\{1 - \frac{h + r - (r^2 - a^2)^{1/2}}{[r^2 + (r+h)^2 - 2(r+h)(r^2 - a^2)^{1/2}]^{1/2}}\right\}, \tag{9a}$$

$$E_{0r} = \frac{a^2\sigma_r}{2\varepsilon_0}\left\{[r^2 + (r+h)^2 - 2(r+h)(r^2 - a^2)^{1/2}]^{-3/2}\right.$$

$$\left. + \frac{\varepsilon_r - 1}{\varepsilon_r + 1}[r^2 + (r+h+L)^2 - 2(r+h+L)(r^2 - a^2)^{1/2}]^{-3/2}\right\}. \tag{10a}$$

In order to account for the effect of dipole discreteness, we will use the equation in [11]:

$$\overline{E}_{0g} = \frac{\overline{\mu}_r}{2\varepsilon_0 a_*^2 l_0}\sum_{K_1K_2}\exp(-Kz)[1 - \exp(-Kl)],$$

where

$$K = \frac{2\pi}{a_*}(K_1^2 + K_2^2)^{1/2};\ K_1,\ K_2 - 1,\ 2,\ 3,\ \ldots$$

Let us now move the origin of coordinates to the center of a dipole and consider also the field due to the mirror image of the lattice. In its final form, the equation will then be

$$\overline{E}_{0g} = \frac{\overline{\mu}_r}{\varepsilon_0 a_*^2 l_0}\sum_{K_1K_2}\left[1 + \frac{\varepsilon_r - 1}{\varepsilon_r + 1}\exp(-KL)\right]\exp(-Kz)\,\mathrm{sh}\,\frac{Kl_0\overline{\cos\theta}}{2}. \tag{11}$$

Inserting (10) and (11) into (2), we obtain the sought expression for the field intensity due to a domain on the z axis in vacuo. In the presence of an adsorption film the field intensity will not be the same on both sides of the interface boundary, because of the additional interaction between adsorbed molecules and the adsorption film. Namely, inside the film the field intensity is lower while above the film it is higher than $\overline{E}_0$. It is impossible to establish a simple relation between the field intensity in a nonhomogeneous medium, because $\overline{E}$ depends not only on the field but also on the geometry of the medium. The system of differential equations of electrostatics together with the condition of potential continuity at the boundary will, however, relate the characterizing field quantities at adjacent points and will be valid in any medium [12]. On this basis, one can obtain a relation for the field intensity on both sides of the interface between an adsorption film and its vapor:

$$E_0' = E_0\frac{2}{\varepsilon' + \varepsilon''}, \tag{12}$$

$$E_0'' = E_0\frac{2\varepsilon'}{\varepsilon''(\varepsilon' + \varepsilon'')}. \tag{13}$$

The field intensity due to a domain depends on the temperature (see [13], for example), according to expression (10), because m (z-component of the dipole moment μ) in the expression for the dipole density $\sigma = m/a_*^2$ is a function of the temperature [14]. With equal probabilities of all dipole orientations in a force field, the mean statistical value for the potential energy of a dipole is expressed as

$$\langle \overline{\Pi} \rangle = \frac{\int_0^{\nu_0} \Pi \exp\left(-\frac{\Pi}{kT}\right) d(\cos\theta)}{\int_0^{\nu_0} \exp\left(-\frac{\Pi}{kT}\right) d(\cos\theta)}. \tag{14}$$

Since $m = \mu\overline{\cos\theta}$, hence the integrals in (14) yield

$$\overline{\cos\theta} = \frac{1 - \cos\nu_0}{2}\left\{\mathrm{cth}\left[\frac{X}{2}(1 - \cos\nu_0)\right] - \frac{1}{\frac{X}{2}(1 - \cos\nu_0)} + \frac{1 + \cos\nu_0}{1 - \cos\nu_0}\right\}, \tag{15}$$

with the dimensionless parameter $X = uE/kT$. For an adsorbate molecule free in space we have $\nu_0 = \pi$. Then

$$m = \mu\left(\mathrm{cth}\,X - \frac{1}{X}\right). \tag{16}$$

For a radical on the adsorbent surface, free inside a cone with the vertex angle $2\nu_0 = \pi$ (free in a half-space) we have

$$m_r = \frac{\mu_r}{2}\left(\operatorname{cth}\frac{X_r}{2} - \frac{2}{X_r} + 1\right), \tag{17}$$

with $X_r = \mu_r E_r/kT$.

Here E_r is calculated by a summation of the field intensity vectors E_{ri} of all surface radicals in a domain and their mirror images, in accordance with formula (3).

The energy of dispersive interaction between an adsorbed molecule and all volume elements of the sorbent is calculated according to the conventional formula in [16]. Disregarding quadrupole and quadrupole-quadrupole components of interaction, we have for an infinite plane

$$\varphi_{\text{disp}} = \frac{\pi C N_r}{6z^3}. \tag{18}$$

Equation (18), derived by integrating the energy of pairwise dispersive interaction over the entire sorbent volume, is rigorously valid when $z \gg d$ (d denoting the linear dimension of a dipole molecule). At small distances z it becomes necessary to take into account the discreteness of the sorbent medium. According to the data in [17], a summation of the interaction energies of volume elements in the sorbent will yield higher values for φ_{disp} than formula (18).. For organic compounds with the linear dimension $d = 4.6$ Å this value is approximately 3.0 times higher at $z = d$ and 1.5 times higher at $z \simeq 3d$; at distances $z > 5d$ summation and integration yield approximately the same results. With this in mind, we can now obtain an approximate but more accurate relation for the energy of dispersive interaction as a function of z:

$$\varphi_{\text{disp}} = \frac{\pi C N_r}{6z^3}\left[1 + \exp\left(A + Bz^4\right)\right], \tag{19}$$

where

$$A = \frac{4}{5}; \quad B = -\frac{20}{9}\cdot 10^{27}, \text{ cm}^{-4}.$$

The adsorption potential of the adsorbent field can be calculated, therefore, if the nature of both sorbent and sorbate are known as well as the electric-field topography of the surface. With (16) taken into account expression (1) becomes finally

$$\varphi = kT\left(X\operatorname{cth}X - 1 + \frac{2\pi\varepsilon_0 kT\alpha}{\mu^2}X^2\right) + \varphi_{\text{disp}}. \tag{20}$$

The last expression is used for calculating the thermodynamic parameters of adsorption films of polar liquids at equilibrium and for formulating the equations of state of moist materials.

NOTATION

m	is the component of the dipole moment of a molecule (or radical) in the direction of the field;
θ	is the angle between dipole axis and the direction of the field;
ε_0	is the dielectric constant;
ε	is the relative dielectric permittivity of sorbent;
R	is the distance from given point to the dipole;
ψ	is the field potential;
σ	is the surface charge (or dipole) density;
a_*	is the parameter of the domain lattice;
a	is the linear dimension of the domain;
L	is the distance from center of the dipole of a radical to its mirror image;
ν_0	is the angle of maximum dipole twist from its mean orientation;
h	is the thickness of the adsorption film;
l_0	is the length of the dipole;
μ	is the dipole moment of a molecule (or radical);
Π	is the potential energy of a molecule in the adsorbent field;
k	is the Boltzmann constant;
T	is the temperature;
$\overline{\cos\theta}$	is the mean statistical value of $\cos\theta$;

C is the London constant;
N_r is the number of molecules per unit sorbent volume.

Subscripts

r refers to the sorbent.

Superscripts

$'$ refers to the adsorption film;
$''$ refers to the vapor phase.

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