THE JOURNAL OF CHEMICAL PHYSICS   VOLUME 39, NUMBER 2   15 JULY 1963

Work Function Change on Monolayer Adsorption

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(Received 4 February 1963)

A self-consistent treatment is presented of the change in work function, or surface potential, produced by the adsorption of an immobile or mobile regular array of adsorbate entities on a plane (usually conducting) adsorbing surface. The adsorbed entities may be polarizable atoms, ions, or molecules, and the molecules and ions may have orientable permanent dipole moments, not assumed fixed in direction. The depolarizing field at a given adsorbed element arising from the total polarization of all its surrounding elements is taken into account in all cases, as is the possible presence of an average charge on the adsorbing surface. A distinction is introduced between the "natural" field polarizing a single adsorbate entity and the similar effective field leading to some time-average permanent dipole polarization. General formulas for surface potential in terms of surface charge and surface coverage are derived for all cases and compared with earlier, less general treatments of the same cases. The results are applied to electrolyte double-layer measurements and surface-potential determinations.

I. INTRODUCTION

A NUMBER of different expressions have been given for the change produced in the work function of a material by adsorption of a complete or partial monolayer thereon. Many of these expressions are quite approximate, some are often incorrectly applied, and others are only pertinent to certain systems whose physical properties are not always clearly delineated. It is therefore appropriate to review the situation, analyze certain frequently occurring situations, and present more general and less approximate expressions for work function change (WFC) in these cases.

Although we are primarily concerned with the WFC on adsorption of an excellent or reasonably good conducting surface, some of the following results apply to adsorption on a dielectric surface as well. The "true work function" of a uniform metallic surface is defined as the work necessary to remove an electron from the surface of the metal to infinity at 0°K.[1-3] We are here concerned with the effective work function, an average over the entire surface at the measuring temperature. Since the adsorbed layer is composed of discrete entities, its properties will vary rapidly with lateral position along the surface. The way these properties are averaged in a determination of the WFC depends upon the specific measuring technique. The average will be arithmetical when the effective WFC is determined from a contact potential difference measurement using a macroscopic device such as a vibrating metallic probe near the adsorbed surface. In this case, it is always arranged that the probe is separated from the surfaces by a distance small compared to the lateral dimensions of the adsorbent and large compared with adsorbed-layer thickness and the average separation of individual adsorbed entities. An ordinary average is also obtained from differential capacitance measurements in electrolytic solutions where the electrode with the adsorbed layer of interest is one "plate" of a capacitor and the other is formed by a diffuse layer of ions parallel thereto.

On the other hand, in thermionic and high-field emission an ordinary average is inappropriate since the measured current is principally emitted from microscopic surface regions of lowest work function: locations where adsorption has lowered the work function or those where there is no adsorbate when adsorption increases the work function. To deal with these cases properly, a task which is not attempted herein, one must consider the detailed lateral and perpendicular variation of electrostatic potential in the immediate neighborhood of adsorbed elements and carry out the appropriate averaging to obtain the macroscopic measured current.

[1] C. Herring and M. H. Nichols, Rev. Mod. Phys. **21**, 185 (1949).

[2] R. V. Culver and F. C. Tompkins, Advan. Catalysis **11**, 74–79 (1959).

[3] E. P. Gyftopoulos and J. D. Levine, J. Appl. Phys. **33**, 67 (1962).

The measured current is principally emitted from surface regions where adsorption has lowered the work function. To deal with these cases properly, a task which is not attempted herein, one must consider the detailed lateral and perpendicular variation of electrostatic potential in the immediate neighborhood of adsorbed elements and carry out the appropriate averaging to obtain the macroscopic measured current.

For present purposes, it is convenient to define the effective WFC upon adsorption as the effective work function after adsorption has occurred minus that prior to adsorption. We also express the effective work function in terms of an electrostatic potential V whose zero will be taken at infinity.[4] Thus, a decrease in V at the adsorbent surface upon adsorption of a dipole layer is equivalent to a decrease in the effective work function of the surface. Let ΔV therefore be the change in potential of the surface, averaged over the surface, corresponding to the effective WFC on adsorption of a partial or complete monolayer of material different from the adsorbent. The adsorbent will be taken as a conducting plane, smooth like the surface of liquid mercury far below its boiling point.

The plan of the present paper is as follows. We first classify those situations which are to be considered in terms of the electrical properties of the adsorbate. Next, brief discussions are given of prior analyses of these situations, and finally a more general analysis is presented. This work includes the effects of a nonzero average adsorbent surface charge, orientable permanent dipoles, induced and image dipoles, and effects of interaction in the plane between the discrete adsorbed elements.

GLOSSARY OF SYMBOLS

A	$4\pi N_s \alpha / d_1$
b	$9\alpha N_s^{\frac{3}{2}}$
d	Effective thickness of an adsorbed element
d_1	Effective distance between charge centroid of an adsorbed ion and the surface of adsorbent
E	Electric field normal to adsorbent surface averaged through thickness d and averaged over adsorbent surface
$\mathcal{E}_1$	$\mathcal{E}_{n_1} + \mathcal{E}_{eff}$; self-consistent effective field leading to induced polarization perpendicular to adsorbent surface
$\mathcal{E}_2$	$\mathcal{E}_{n_2} + n^{-2}\mathcal{E}_{eff}$; self-consistent effective field leading to permanent dipole orientation perpendicular to adsorbent surface
$\mathcal{E}_d$	Self-consistent, time-average depolarizing field
$\mathcal{E}_{n_1}$	Effective field leading to induced polarization of a single isolated adsorbed element in the absence of average charge on the adsorbent

$\mathcal{E}_{n_2}$	Effective field orienting a single, isolated adsorbed dipolar element in the absence of average charge on the adsorbent
$\mathcal{E}_{eff}$	$4\pi q + \mathcal{E}_d$
e	Magnitude of electronic charge
k	Boltzmann's constant
N	Number of adsorbed entities per unit area
N_s	Maximum value of N
N_v	$\theta N_s / d$; number of adsorbed entities per unit volume in the thickness d
n	Index of refraction of bulk adsorbate
$\mathcal{P}$	$\mathcal{P}_1 + \mathcal{P}_2$; total average polarization in layer of thickness d
$\mathcal{P}_1$	Average induced polarization in layer of thickness d
$\mathcal{P}_2$	Average permanent dipole polarization in layer of thickness d
q	Average charge density of adsorbent surface
q_a	$\theta N_s z e$; average adsorbate layer charge density
q_n	Average charge density of adsorbent surface in absence of charge sharing of adsorbate particles with adsorbent surface
T	Absolute temperature
V	Electrostatic potential at adsorbent surface referred to infinity
V_1	$E(q, \mathcal{P})d = 4\pi q d - 4\pi \mathcal{P} d$; potential difference across layer of thickness d
ΔV	$E(q_2, \mathcal{P})d - E(q_1, 0)d$; difference in potential at adsorbent surface when its charge density is q_2 and adsorbed layer is present and that when surface charge density is q_1 and no adsorbed layer is present. The charge densities q_1 and q_2 are sometimes independently controllable; otherwise, their relation is determined by the type of experiment
z	Effective valence of an adsorbed entity
z_n	Valence of an isolated adsorbate entity
WFC	Effective work function change on adsorption
α	Polarizability of an adsorbed species
β	Proportionality constant appropriate when $\lvert \mathcal{E}_2 \rvert \ll (kT/\mu)$
γ	1 in the case of mobile adsorbate elements and θ for the immobile case
δ	1 in the case of mobile adsorbate elements and $\theta^{-\frac{1}{3}}$ for immobile elements
ϵ_{eff}	Quantity playing the role of an effective microscopic dielectric constant for a two-dimensional array of polarizable entities
ϵ_∞	Bulk value of the high-frequency dielectric constant of adsorbate material, $\geq n^2$
θ	N/N_s; fractional coverage of available surface
Λ	8.894 for hexagonal array; 9.034 for square array. Generally set equal to 9
μ	Magnitude of permanent dipole moment; may be field-dependent

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[4] A glossary of symbols follows the Introduction.

$\mu_\perp$ Magnitude of permanent-dipole-moment component perpendicular to adsorbent surface

$\langle\mu(\mathcal{E}_2)\rangle$ Time-average value of normal component of permanent dipole moment when the average orienting field is $\mathcal{E}_2$

σ 11.034 for a hexagonal array; 9.034 for a square array

II. CLASSIFICATION AND DISCUSSION OF PRIOR WORK

Discrete adsorbed entities may have a variety of properties. An idealized electrical classification is shown in Table I. The adsorbed neutral material may be an atom (Case A) or a molecule or molecular complex (Case C). Only the situation where the charged adsorbent is an ion of effective valency z is considered. The induced polarization will, in general, arise from the electrical forces of adsorption in the absence of any average charge on the conducting adsorbent, from planar interaction, and from the presence, if any, of an average charge density q on the adsorbing surface.

Let N_s be the maximum number per unit area of adsorbed entities possible on the adsorbent and $\theta \equiv N/N_s$ be the average fraction of the available surface actually covered when the surface density is N. By definition, the condition $\theta = 1$ is considered that for a complete monolayer. The quantity N_s may be either the number of available adsorption sites per unit area or may be directly determined by the size of adsorbate entities and the degree to which they can be close packed on the adsorbent surface.

In the neutral situation, the usual case considered is B even though all adsorbents have some polarizability. It is frequently assumed that the dipoles are aligned with their permanent dipole moments, of magnitude μ, perpendicular to the surface. When this restriction is relaxed, it is alternatively usually assumed that the component of μ normal to the surface, $\mu_\perp$, is a constant independent of θ and of average charge on the surface. Then elementary electrostatics applied to a continuous dipole sheet leads to[2,5-7] the Helmholtz

formula

$$\Delta V = \pm 4\pi\theta N_s\mu_\perp, \tag{1}$$

where the minus sign is appropriate when the positive pole of the dipole lies away from the surface. This result must be modified,[8-10] as shown later, because of the polarizability of real dipoles and their discrete nature, which causes a depolarizing field at the position of a given dipole arising from all surrounding dipoles. Only in the nonphysical Case B is Eq. (1) really appropriate for permanent dipoles.

Equation (1) is sometimes[11,12] written with a 2π factor instead of 4π. This is incorrect for Case B, although Devanathan[12] has used the 2π in this case. It is correct in Case D, as shown by Langmuir,[11] if the adion is perfectly imaged in a conducting surface and the magnitude of the effective dipole moment, $\mu = \mu_\perp$, is taken as $|ze|$ times the distance $2d_1$ between the charge centroid and its image.[2,6,7,13] If the distance d_1 from charge centroid to the "surface" is used in defining μ, then the factor 4π is again appropriate. Any real ion will be polarizable, however; then Case E or G is applicable and planar-interaction depolarization effects must be taken into account. Note that when $z = 0$, Case E reduces to Case A.

When the adsorbing surface is a good conductor, it is appropriate to consider imaging of all charges of discrete adsorbate elements in this surface. This is usually done for ionic charges, as above, but dipole imaging is almost invariably neglected. Accordingly, we neglect the effects of imaging dipoles, both permanent and induced, in the adsorbing surface. This approximation may only be judged in the context of a specific distance between the adsorbed entities and the surface compared with the average planar interparticle distance, and it approaches exact validity as this ratio increases. Concerning the effect of dipole imaging upon the local electric field producing polarization, however, it has been shown[14] that frequently this effect on polarization is small. Presumably the effect on the potential is also small under most physical conditions. Its neglect is correct to roughly the same order as is the neglect of the higher moments of the adsorbate. It may be taken into account, however, at least to first order, by considering that it produces a small multiplicative increase in the total polarizability.

TABLE I. Classification of the adsorbate.

Polarization possibilities→ Charge condition ↓	No moment	Induced dipole moment	Permanent dipole moment	Permanent and induced polarization
Neutral	···	A	B	C
Charge: ze	D	E	F	G

[5] J. H. de Boer, *Electron Emission and Adsorption Phenomena* (Cambridge University Press, Cambridge, England, 1935), p. 85.
[6] J. H. de Boer, Advan. Catalysis **8**, 118 (1956).
[7] I. Higuchi, T. Ree, and H. Eyring, J. Am. Chem. Soc. **79**, 1330 (1957).

[8] J. K. Roberts, *Some Problems of Adsorption* (Cambridge University Press, London, 1939).
[9] A. R. Miller, Proc. Camb. Phil. Soc. **42**, 292 (1946); *The Adsorption of Gases on Solids* (Cambridge University Press, Cambridge, England, 1949), pp. 112–113.
[10] Reference 6, pp. 121–123.
[11] I. Langmuir, J. Am. Chem. Soc. **54**, 2798 (1932).
[12] M. A. V. Devanathan, Proc. Roy. Soc. (London) **A264**, 133 (1961).
[13] Under some circumstances, it is desirable to refine the definition of d_1 over that given herein.
[14] J. R. Macdonald and C. A. Barlow, Jr., J. Chem. Phys. **36**, 3062 (1962).

Equation (1) applies to Cases B and D only when planar interaction is neglected. All real adsorbates are polarizable, however, and a number of authors[7,12,15-20] have attempted to include such polarizability by the macroscopically inspired introduction of a dielectric constant, here termed ϵ_∞, in Eq. (1). The result may be written

$$\Delta V = \pm 4\pi\theta N_s \mu_\perp / \epsilon_\infty, \qquad (2)$$

where ϵ_∞ includes no contribution from permanent dipolar polarization. Sometimes[12,17-19] ϵ_∞ is taken to be the macroscopic, nonpolar dielectric constant of the surroundings of the adsorbent elements (e.g., in electrolyte double-layer work where the surrounding material may be made up of water molecules and the adsorbed entity in question may be an organic molecule having a permanent dipole moment) and sometimes[16,20] it is taken to be that of the adsorbate material itself. Neither assumption is good since insofar as the introduction of ϵ_∞ at all is valid it must be a θ-dependent function of the properties of both the adsorbate and its surroundings; furthermore, the use of macroscopic quantities in a microscopic system is inappropriate, as noted below.

Equation (2) may be readily derived from Gauss' law if $\mu_\perp$ is written as $e_1 d$, where d is here the normal component of the separation of charges $\pm e_1$. If it is now assumed that the material between these charges has a dielectric constant ϵ_∞ and the discrete charges are smeared in their planes, Eq. (2) immediately follows. This treatment allows no account to be taken of discrete planar interaction effects and further makes the definition of ϵ_∞ uncertain. It has been rejected by Harkins and Fischer[21] primarily because of the application of macroscopic concepts to a microscopic situation. An improved microscopic treatment is outlined in the next section. Note that the ΔV defined herein has the same sign as the WFC, is equivalent to the "surface potential" of Harkins and Fischer,[21] and is the same in magnitude and opposite in sign to the surface potential of Culver and Tompkins.[2]

Higuchi, Ree, and Eyring[15] have given an approximate calculation of ϵ_∞ in Case E. They assume that the average field in the adsorbed layer is also the local field acting on a small volume element to induce polarization. This leads to the usual Laplace–Debye result, $\epsilon_\infty = 1 + 4\pi N_v \alpha$, where N_v, given by the above

authors as $\theta N_s / d_1$, is the number of adions per unit volume, α the ionic polarizability—taken independent of θ, $\mu_\perp$ in (2) is $|ze| d_1$, and d_1 is again the distance between charge centroid and a metallic surface. Again, no planar interaction effect is directly included. Other authors have made the even less satisfactory assumption that for Eq. (2) ϵ_∞ is a constant $\geq n^2$, whereas n^2 is the square of the index of refraction of either the adsorbate material in bulk or of the surrounding material. The equals sign above is used when it is expected that only electronic polarization is important, the greater-than-equals when librational effects, as in a vibrating adsorbed molecule, are also deemed contributory. The uncertainty in the formula to use for ΔV, in ϵ_∞, and even in whether $\mu_\perp$ is the full permanent dipole moment or not, makes an equation such as (2) hazardous to use in calculating μ from ΔV data.

Case A has been considered for adsorption of strontium and barium adatoms on tungsten by Moore and Allison.[22] The adatoms are assumed to be polarized by local surface electric fields, and dipolar planar interaction of the resulting dipoles is taken into account. Equation (1) was used with $\pm \mu_\perp \equiv -\alpha E$, where E is the total polarizing field including a depolarization contribution. The use of Eq. (1) with the above $\mu_\perp$ is appropriate in Case A if there is zero average charge on the adsorbent metal. Field saturation of α was assumed by writing $\alpha = \alpha_0 - kE$, where k is here a saturation constant. Since one expects saturation to be an even function of E, it would have been better to write $\alpha = \alpha_0 - kE^2$. It is well to point out here that there is little agreement whether adsorbed metal atoms on metals such as tungsten should be considered as polarized atoms, positive ions, or a mixture of both.[3,7,11,15,22]

Both the above treatment and the recent one of Gyftopoulos and Levine[3] are concerned with thermionic emission. Both use an effective WFC averaged over the surface in the ordinary way to compare with work function changes derived from emission current. The latter authors introduce an interesting refinement consisting of an electronegativity barrier at the metal surface dependent on surface coverage θ. When $\theta = 1$, they take the effective work function of the resulting surface to be that of an ordinary bulk layer of the adsorbed material (Cs, Sr, or Th). This assumption is discussed further later; it seems dubious since it appears that usually the properties of a monolayer differ at least somewhat from those of the bulk material.[23] As already mentioned, there is doubt concerning the detailed applicability to the thermionic emission situation of a treatment of the WFC based on ordinary averaging over the surface. Finally, the excellent agreement between theory and experiment obtained by Gyftopoulos and Levine is at least in part a consequence

[15] I. Higuchi, T. Ree, and H. Eyring, J. Am. Chem. Soc. 77, 4969 (1955).

[16] F. W. Schapink, M. Oudeman, K. W. Leu, and J. N. Helle, Trans. Faraday Soc. 56, 415 (1960).

[17] R. Parsons, Proc. Roy. Soc. (London) A261, 79 (1961).

[18] R. J. Watts-Tobin, Phil. Mag. 6, 133 (1961).

[19] N. F. Mott and R. J. Watts-Tobin, Electrochim. Acta 4, 79 (1961).

[20] R. S. Hansen, R. E. Minturn, and D. A. Hickson, J. Phys. Chem. 61, 953 (1957).

[21] W. D. Harkins and E. K. Fischer, J. Chem. Phys. 1, 852 (1933).

[22] G. E. Moore and H. W. Allison, J. Chem. Phys. 23, 1609 (1955).

[23] J. H. de Boer, Advan. Colloid Sci. 3, 50–51 (1950).

of fitting a smooth curve with (roughly) a polynomial of somewhat arbitrary form. Fitting is often further complicated by doubt concerning the surface coverage which corresponds to exactly $\theta = 1$.

III. ANALYSIS OF THE GENERAL SITUATION

Introduction

Let us consider an adsorbed layer of adsorbate thickness d. This quantity is taken as the extension of the individual adsorbed entities, all of a single species, normal to the adsorbing surface and may vary somewhat with average electric field strength in the layer because of possible electrostriction, compression, and permanent dipole orientation effects.[14,24] The adsorbate is also assumed to have a homogeneous polarizability α which may possibly decrease somewhat with field magnitude. Finally, assume that the individual elements may have a permanent dipole moment μ, whose average component normal to the surface may vary with effective orienting field as the dipole orientation changes, and/or an effective dipole moment arising from an adion and its image in a conducting absorbent. By using individual-element polarizability and dipole moment, as is appropriate in a microscopic treatment, we avoid the need to introduce ordinary dielectric constants, which are macroscopic properties.

For adsorbed molecules or ions with permanent dipole moments, let us write $\pm \mu_\perp = - \langle \mu(\mathcal{E}_2) \rangle$, where $\langle \ \rangle$ denotes a time average over all dipolar elements. The effective orienting field $\mathcal{E}_2$ and the form of the above relation are discussed later. In general, adsorbed entities will be free to rotate to a greater or lesser extent and, depending on available thermal energy and the magnitude of $\mathcal{E}_2$, will rotate through all available orientations. Only the average normal component of the permanent dipole moment $\langle \mu(\mathcal{E}_2) \rangle$, a quantity having the same sign as $\mathcal{E}_2$, will be of importance in the present situation.

The present microscopic, discrete-element treatment will only be applicable to the cases where the adsorbent surface is close packed with adsorbate entities of a single species ($\theta = 1$) or, when $\theta < 1$, the space between such elements adsorbed on the surface is unoccupied. This is not the case in some electrolyte situations, when two different gases are simultaneously adsorbed on the same surface, or when ions and atoms of the same element are simultaneously present on the adsorbing surface. A complicated electrolyte situation whose approximate treatment has been briefly outlined elsewhere[24] is that where organic dipolar molecules are specifically adsorbed on a mercury electrode. When $\theta = 0$, the electrode is covered by a close-packed monolayer of water molecules. For $0 < \theta < 1$, each adsorbed organic molecule (which has displaced one or more

water molecules on the electrode) interacts both with other such molecules and with neighboring water molecules. Such interaction between two adsorbed species having different properties is beyond the scope of the present treatment.

Polarizability α

The ionic, atomic, or molecular polarizability of an adsorbed entity may be expected to differ somewhat from the polarizability of the same material in bulk since polarizability is a property which depends to some degree on the surroundings of the entity in question.[25,26] In the present work, however, we take α independent of θ, and, as a first approximation for atoms and molecules, use the bulk value

$$\alpha \simeq (3/4\pi)(\epsilon_\infty - 1)/N_v(\epsilon_\infty + 2), \qquad (3)$$

where N_v and ϵ_∞ here pertain to bulk. A slightly better approximation[24] may be to use the N_v value appropriate for an adsorbed layer with $\theta = 1$. An even more approximate expression for α has been given by Gyftopoulos and Levine[3] who also cite evidence suggesting that α for adatoms should include only the electronic polarizability and thus $\epsilon_\infty \simeq n^2$, where n is the bulk refractive index.

The polarizability of alkali metal atoms is much greater than that of the corresponding ions. For some elements, α_{ion} and α_{atom} may be quite comparable, but pertinent data seem lacking for a comparison of, e. g., F^- and F (not F_2).

Natural Fields $\mathcal{E}_{n_1}$ and $\mathcal{E}_{n_2}$

An intense short-range electric field may be expected at the surface of a clean adsorbent.[22,27] This surface field, which will be quite inhomogeneous, will polarize adsorbed entities. In addition, covalent bonding, nonpolar van der Waals' forces, and other adsorption processes may all lead to effects in the adsorbate equivalent to some inhomogeneous polarization of it. Further, if an adsorbed entity is polarized at all, the image of this polarization in a conducting adsorbent will tend to increase the original polarization; as mentioned earlier, this effect may be replaced approximately by an increase in the total polarizability. At the surface of a clean metal there is considerable electron wavefunction overlap[28] which generally acts to induce dipoles in adsorbed elements with the positive pole outwards. All the above effects cooperatively may produce some polarization in an adsorbed ion, atom, or molecule, but it will not be uniform perpendicular

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[24] J. R. Macdonald and C. A. Barlow, Jr., Proceedings, First Australian Conference on Electrochemistry, Sydney, Australia, February, 1963 (to be published).

[25] C. J. F. Böttcher, *Theory of Electric Polarization* (Elsevier Publishing Company, Amsterdam, 1952), pp. 205–208.
[26] R. Yaris and B. Kirtman, J. Chem. Phys. **37**, 1775 (1962).
[27] Reference 23, pp. 9, 36.
[28] R. Stratton, Phil. Mag. **44**, 1236 (1953); N. G. McCrum and J. C. Eisenstein, Phys. Rev. **99**, 1326 (1955); J. C. P. Mignolet, Discussions Faraday Soc. **7–8**, 105 (1949–50); *Chemisorption*, edited by W. E. Garner (Academic Press Inc., New York, 1957), pp. 118–120; Bull. Soc. Chim. Belges **64**, 126 (1955); Ref. 2, p. 73.

to the adsorbing surface. Let us, therefore, introduce an average natural field $\mathcal{E}_{n1}$, normal to the surface and taken uniform through the thickness d, which, together with the effective polarizability, produces the same average polarization as all the above effects taken together. Note that this field is defined in the absence of average charge on the adsorbent and should be almost independent of q and absolute temperature. We take $\mathcal{E}_{n1}$ completely independent of q and consider it as a parameter to be determined from fitting of theory and experiment. When $\mathcal{E}_{n1}$ is positive, the induced dipole will have its positive pole outwards from the surface.

The effective field $\mathcal{E}_{n1}$ is that which produces the same average induced polarization (in the absence of planar interaction) at $q=0$ as does the actual surface field (for $\theta\to0$), a quantity which varies rapidly in all three dimensions. The average polarization $\mathcal{P}_{n1}$ associated with $\mathcal{E}_{n1}$ is related to the local induced polarization, $\mathcal{P}_{n1\,loc}(x)$, averaged in the plane but varying in the $+x$ direction normal to the surface, by

$$\mathcal{P}_{n1}=d^{-1}\int_0^d \mathcal{P}_{n1\,loc}(x)\,dx. \qquad (4)$$

This average polarization is itself related to the average potential difference across the thickness d in a simple manner discussed in a later section. Note that $\mathcal{E}_{n1}$ is defined in the absence of planar interaction and so is independent of θ.

Next, consider the effective dipole orienting field $\mathcal{E}_{n2}$, a part of the field $\mathcal{E}_2$ already introduced. Again, $\mathcal{E}_{n2}$ is defined at $q=0$ and should be nearly independent of both q and absolute temperature. It is the fictitious normal field which would produce the actual time-average orientation of the permanent dipole of a single average adsorbed element, $\langle\mu(\mathcal{E}_{n2})\rangle$, appropriate at $q=0$ and $\theta\to0$. We assume $\mathcal{E}_{n2}$ independent of both q and θ. As in the case of $\mathcal{E}_{n1}$, $\mathcal{E}_{n2}$ is dependent on both the character of the adsorbent and that of the adsorbate. It is associated with the local, inhomogeneous surface electric field, and with "chemical" and steric effects. There is no reason to expect that $\mathcal{E}_{n1}$ and $\mathcal{E}_{n2}$ be equal since they arise in part from different causes and involve different quantum-mechanical interactions with the adsorbent. For example, some average orientation of a permanent dipole molecule will occur because the molecule is nonspherical, because the dipole may not be localized at the center, because covalent bonding, if present, will occur with the permanent dipole in a certain orientation, etc. It even appears that under some conditions $\mathcal{E}_{n1}$ and $\mathcal{E}_{n2}$ may be of opposite sign.[29] The quantity $\mathcal{E}_{n2}$ is perhaps most familiar in electrolyte double-layer theory where it has played a role for some time.[30]

Finally, note that the fields $\mathcal{E}_{n1}$ and $\mathcal{E}_{n2}$ each affect the polarization of both permanent and induced type through the interaction between such polarization. For example, even in the absence of a finite $\mathcal{E}_{n2}$, if $\mathcal{E}_{n1}\neq0$ there will be a nonvanishing value of $\langle\mu\rangle$ at $q=0$ arising from the contribution of the finite induced dipole moment to the electric field $\mathcal{E}_2$. This becomes clear in the next sections.

Polarizing and Orienting Fields $\mathcal{E}_1$ and $\mathcal{E}_2$

When q and θ are nonzero, the polarizing and orienting fields, $\mathcal{E}_1$ and $\mathcal{E}_2$, respectively, differ from $\mathcal{E}_{n1}$ and $\mathcal{E}_{n2}$. Let $\mathcal{E}_{eff}$ be the time-average electric field, taken constant through the thickness d, at the position of a given adsorbed entity arising directly from the average charge on the electrode and from the depolarizing effect of all surrounding polarized elements. Denoting the depolarizing field by $\mathcal{E}_d$, we then have

$$\mathcal{E}_{eff}=4\pi q+\mathcal{E}_d, \qquad (5)$$

and we may write

$$\mathcal{E}_1=\mathcal{E}_{n1}+\mathcal{E}_{eff}. \qquad (6)$$

The average induced polarization $\mathcal{P}_1$ is then

$$\mathcal{P}_1=N_v\alpha\mathcal{E}_1, \qquad (7)$$

where $N_v\equiv\theta N_s/d$, not $\theta N_s/d_1$.

The field $\mathcal{E}_2$ must be formed slightly differently. By definition, $\mathcal{E}_{n2}$ contributes directly to it. On the other hand, $\mathcal{E}_{eff}$ does not act directly on a given dipole since the dipole will be screened by surrounding charge. This screening will almost certainly be a function of dipole orientation but, as a first approximation, is here represented by n^2, the electronic contribution to the high-frequency dielectric constant. An improved approximation should include the dependence of the screening factor on monolayer density.[24] These considerations lead to

$$\mathcal{E}_2\cong\mathcal{E}_{n2}+n^{-2}\mathcal{E}_{eff}. \qquad (8)$$

It would be possible to redefine $\mathcal{E}_{n2}$ so that a shielding factor would be necessary multiplying it as well as $\mathcal{E}_{eff}$. This would be the preferable procedure if shielding varied with orientation but is unnecessary here where it is taken independent. The polarization $\mathcal{P}_2$ associated with $\mathcal{E}_2$ is

$$\mathcal{P}_2=N_v\langle\mu(\mathcal{E}_2)\rangle. \qquad (9)$$

For a simple two-state model in which the dipole moment may be only parallel or antiparallel to the surface normal, $\langle\mu(\mathcal{E}_2)\rangle=\mu\tanh[(\mu/kT)\mathcal{E}_2]$, while if all orientations are allowed, $\langle\mu(\mathcal{E}_2)\rangle=\mu L[(\mu/kT)\mathcal{E}_2]=\mu[\coth\{(\mu/kT)\mathcal{E}_2\}-\{(\mu/kT)\mathcal{E}_2\}^{-1}]$, where L is the Langevin function. For small argument, let us write in general $\langle\mu(\mathcal{E}_2)\rangle\to\beta\mathcal{E}_2$ as $\mathcal{E}_2\to0$, where β depends on the details of the possible orientations permitted by steric and other effects and is just $(\mu^2/3kT)$ in the

[29] J. H. de Boer, *The Dynamical Character of Adsorption* (Oxford University Press, London, England, 1953), p. 169.

[30] References 14 and 24 and references given therein. In these papers $\mathcal{E}_{n2}$ is designated as E_0 and $\mathcal{E}_n$, respectively.

Langevin case. In the above two examples $\langle\mu(\mathcal{E}_2)\rangle\rightarrow\mu$ as $\mathcal{E}_2\rightarrow\infty$, but the limit may be a lesser value if perpendicular dipole orientation is not permitted.

Depolarizing Field $\mathcal{E}_d$

In calculating the depolarizing field, it is necessary to make an assumption about the distribution in the plane of discrete adsorbed elements. Let us consider two situations, (a) that where the discrete entities are immobily adsorbed (at random in the small but uniformly in the large) on a proportion θ of a hexagonal or square array of N_s sites, and (b) that where adsorbed entities are mobile and at every θ value arrange themselves in a regular hexagonal or square array whose spacing depends on θ. This last situation is reasonable for mobile elements at not too low θ since mutual dipolar repulsion will tend, on the average, to make each element move as far as possible away from each of its neighbors. Langmuir[11] has calculated the effect of thermal motion in the plane of the adsorbed elements. As usual, it is neglected here.

In general, the time-average depolarizing field arising from surrounding dipoles may be written as[24]

$$\mathcal{E}_d = -[\alpha\mathcal{E}_1 + \langle\mu(\mathcal{E}_2)\rangle]\gamma\sum_i r_i^{-3}, \tag{10}$$

where r_i is the distance between a selected entity and the ith element of the planar array and the summation includes all elements but that selected. Equation (10) must be modified for Case G, that of polarizable ions having permanent dipole moments; this situation is analyzed in the last section. The quantity γ is unity in the mobile case but θ in the immobile because only this fraction of the total sites is then occupied.[9] The nearest-neighbor distance r_1 in Case (a) is $(\frac{4}{3})^{\frac14}N_s^{-\frac12}$ or $N_s^{-\frac12}$ for a hexagonal or square array, respectively. In Case (b), $N_s^{-\frac12}$ is replaced by $(\theta N_s)^{-\frac12}$, where N_s is here the maximum number per unit area allowed. Topping[31] has shown that for an infinite plane array

$$\sum_i r_i^{-3} = \sigma r_1^{-3}, \tag{11}$$

where $\sigma = 11.034$ for a hexagonal array and 9.034 for a square array.

We may now combine the above results to obtain

$$\mathcal{E}_d = -[\alpha\mathcal{E}_1 + \langle\mu(\mathcal{E}_2)\rangle]\Lambda\delta(\theta N_s)^{\frac32}, \tag{12}$$

where $\delta = 1$ for the mobile case and $\theta^{-\frac12}$ for the immobile. The quantity Λ equals $(\frac34)^{\frac12} 11.034 = 8.894$ for a hexagonal array and 9.034 for the square array; thus, which of these two types of arrays is present is unimportant here, and we may take $\Lambda\cong9$.

When $\mathcal{E}_{\mathrm{eff}}$ is formed using (5), (6), and (12), we may solve for $\mathcal{E}_{\mathrm{eff}}$ to obtain

$$\mathcal{E}_{\mathrm{eff}} = [4\pi q - \Lambda\delta(\theta N_s)^{\frac32}\{\alpha\mathcal{E}_{n1} + \langle\mu(\mathcal{E}_2)\rangle\}]/\epsilon_{\mathrm{eff}}, \tag{13}$$

[31] J. Topping, Proc. Roy. Soc. (London) A114, 67 (1927).

where

$$\epsilon_{\mathrm{eff}} \equiv 1 + \alpha\Lambda\delta(\theta N_s)^{\frac32}. \tag{14}$$

Equation (13) is still, in general, an implicit equation for $\mathcal{E}_{\mathrm{eff}}$ since $\mathcal{E}_2$ involves $\mathcal{E}_{\mathrm{eff}}$. The effective "dielectric constant" ϵ_{eff}, which we shall see to some extent takes the place of ϵ_∞ in (2), here arises from a self-consistent, microscopic treatment of planar interaction. It has been primarily used in the past for heat of adsorption calculations rather than in the expression for ΔV. For the mobile adsorbate case, ϵ_{eff} has been given as above by de Boer,[10] while it was introduced by Miller[9] in the immobile case. In this latter case, it is $\epsilon_{\mathrm{eff}}\cong1+9\alpha\theta N_s^{\frac32}$ which does not differ greatly from the result for ϵ_∞ in (2) derived by Higuchi, Ree, and Eyring,[15] namely, $\epsilon_\infty = 1 + 4\pi\alpha\theta(N_s/d_1)$. In typical cases, ϵ_{eff} at $\theta=1$ will lie between 1.1 and 4 in magnitude.

It is perhaps worth mentioning at this point that a treatment of the polarization of a hexagonal array of orientable permanent dipoles which takes into account approximately the correlation between fluctuations in orientation of individual dipoles predicts that at low fields and to first order there is no error produced in average quantities from neglecting fluctuations entirely, as we have done in the above.

Polarization and ΔV. Permanent Dipoles

When Eqs. (6), (7), and (13) are combined, one obtains

$$\mathcal{P}_1 = (\theta N_s)[\alpha\{4\pi q + \mathcal{E}_{n1}\} - (\epsilon_{\mathrm{eff}} - 1)\langle\mu(\mathcal{E}_2)\rangle]/\epsilon_{\mathrm{eff}}d. \tag{15}$$

On combining this result with (9) for $\mathcal{P}_2$, we obtain the total average polarization

$$\mathcal{P} \equiv \mathcal{P}_1 + \mathcal{P}_2 = (\theta N_s)[\alpha\{4\pi q + \mathcal{E}_{n1}\} + \langle\mu(\mathcal{E}_2)\rangle]/\epsilon_{\mathrm{eff}}d, \tag{16}$$

where $\mathcal{E}_2$ is given by

$$\mathcal{E}_2 = \mathcal{E}_{n2} + (n^2\epsilon_{\mathrm{eff}})^{-1}[4\pi q - \Lambda\delta(\theta N_s)^{\frac32}\{\alpha\mathcal{E}_{n1} + \langle\mu(\mathcal{E}_2)\rangle\}]. \tag{17}$$

This is still an implicit expression for $\mathcal{E}_2$, and because $\langle\mu(\mathcal{E}_2)\rangle$ occurs in the expression for $\mathcal{E}_2$, the exact form of the relation between $\langle\mu\rangle$ and $\mathcal{E}_2$ is less important since it is altered by the above negative feedback effect anyway.

We may now write, in terms of average quantities which do not vary through the thickness d or over the surface, the basic equation

$$4\pi q = E + 4\pi\mathcal{P}, \tag{18}$$

where E is the average normal field in the layer. In general, it will be different from $\mathcal{E}_1$ and $\mathcal{E}_2$. The potential difference across d will be $V_1 = Ed$, where V_1 excludes the contribution to V from the adsorbent effective work function, which is taken constant here and thus does not contribute to ΔV. If the charge on the adsorbing surface is made the same after adsorption

as before, it follows that $\Delta V = -4\pi d\mathcal{O}$ or,

$$\Delta V = -4\pi\theta N_s\{[\alpha(4\pi q + \mathcal{E}_{n1}) + \langle\mu(\mathcal{E}_2)\rangle]/\epsilon_{\text{eff}}\}, \quad (19)$$

which may be compared with (1) or (2). In many cases, q will be zero, but this will frequently not be true for thermionic and high-field emission and for the electrolyte double layer. When $q=0$ or constant, Eqs. (19) and (17) predict that for Case C of Table I under some conditions $\langle\mu(\mathcal{E}_2)\rangle$ may decrease as θ increases in part of the θ range, possibly leading to an over-all reduction in ΔV itself.

In Case A, $\langle\mu(\mathcal{E}_2)\rangle\equiv 0$ and (15) becomes

$$\Delta V = -4\pi\theta N_s\alpha(4\pi q + \mathcal{E}_{n1})/\epsilon_{\text{eff}}, \quad (20)$$

which does not differ from (1) when $q=0$ if $\pm\mu_\perp$ is set equal to $-\alpha\mathcal{E}_{n1}/\epsilon_{\text{eff}}$. Although (20) and (2) may seem similar, ϵ_{eff} and ϵ_∞ are really quite different quantities, the first associated with all the planar surroundings of a given adsorbate entity and the latter an averaged property of the bulk material having no direct relation to the adsorbate monolayer.

For Case B, $\alpha=0$ and (19) and (17) become

$$\Delta V = -4\pi\theta N_s\langle\mu(\mathcal{E}_2)\rangle, \quad (21)$$

$$\mathcal{E}_2 = \mathcal{E}_{n2} + n^{-2}[4\pi q - \Lambda\delta(\theta N_s)^{\frac{3}{2}}\langle\mu(\mathcal{E}_2)\rangle]. \quad (22)$$

In the limit of large $\mathcal{E}_2$, $\langle\mu(\mathcal{E}_2)\rangle$ will be a constant and (21) and (1) will be equivalent. Note, however, that the $\langle\mu(\mathcal{E}_2)\rangle$ term in $\mathcal{E}_2$ retards the approach to full orientation, making it more difficult to achieve.

In some cases of practical interest, average orientation of permanent dipoles will be small and $\langle\mu(\mathcal{E}_2)\rangle\cong \beta\mathcal{E}_2$ will be a good approximation. Then an explicit, rather than implicit, solution for ΔV and $\mathcal{E}_2$ may be obtained for Case C. We find,

$$\Delta V = -(4\pi\theta N_s)\frac{[\alpha\{4\pi q + \mathcal{E}_{n1}\} + (\beta/n^2)\{4\pi q + \mathcal{E}_{n2}\}]}{1 + \Lambda\delta(\theta N_s)^{\frac{3}{2}}[\alpha + (\beta/n^2)]}, \quad (23)$$

$$\mathcal{E}_2 = \mathcal{E}_{n2} + \frac{[4\pi q - \Lambda\delta(\theta N_s)^{\frac{3}{2}}\{\alpha\mathcal{E}_{n1} + \beta\mathcal{E}_{n2}\}]}{n^2[1 + \Lambda\delta(\theta N_s)^{\frac{3}{2}}\{\alpha + (\beta/n^2)\}]}, \quad (24)$$

and it is required that $|\beta\mathcal{E}_2/\mu|\ll 1$. In this case, it is clear that the permanent dipole term has led to an increase in ϵ_{eff} over that given by (14); this is a negative feedback effect and may be very appreciable. Note that some of the varied effects and parameters involved in Eq. (19) may be sorted out by carrying out adsorption experiments at a variety of temperatures.[14]

Detailed application of the present results to the electrolyte double-layer problem will be presented elsewhere,[32] but it is worth mentioning that preliminary curve fitting to differential capacitance data yields reasonably good agreement between theory and experiment and indicates that $\langle\mu(\mathcal{E}_2)\rangle/\mu$ for the water monolayer adsorbed on a mercury electrode ($\theta=1$) is

of the order of -0.05 at the electrocapillary maximum (ecm) where $q=0$, and its magnitude is still appreciably less than unity at the extremes of the available electrode charge range where $|q|\sim 20\mu C/cm^2$. Even when $|\langle\mu(\mathcal{E}_2)\rangle/\mu|\gtrsim 0.4$, the approximation $\langle\mu(\mathcal{E}_2)\rangle\cong \beta\mathcal{E}_2$ is still rather good. The maximum value of $|\Delta V|$ calculated from (19) at the extremes of the q range is about 8 V, of which an appreciable fraction is contributed by the nonzero polarizability α. This large value of ΔV is not directly observed in the electrolyte double-layer case, however. There, it is essentially V_1 rather than $\Delta V = -4\pi L d$ which is observable. When $\Delta V = -4\pi\mathcal{O}d$, one may write $V_1 = 4\pi qd + \Delta V$. Curve fitting shows that $|V_1|\ll|\Delta V|$ at the extremes of the experimental q range because $4\pi qd$ and ΔV are always opposite in sign there and comparable in magnitude. Since it is usually the electrode charge, rather than the natural fields, which produces the majority of the polarization when $|q|$ is large, $|4\pi qd|$ will usually exceed $|4\pi\mathcal{O}d|$ at the extremes of the q range.

Polarization and ΔV. Image Dipoles

Equations (16) and (18) are not directly applicable when the dipoles considered are formed by adsorbed ions and their images in a conducting adsorbent. The depolarizing field at a given adsorbed ion arising from all surrounding adsorbed ions and their images may be calculated as before providing the adsorbed ions are not so close together that it is a poor approximation to consider this depolarizing field as arising from ideal dipoles. A somewhat less stringent approximate treatment of the situation for which this assumption is invalid has been given by Mignolet.[33] We use the ideal dipole approximation here with the injunction that the results obtained may require some modification as θ approaches unity.

Since the ion and its image together form the effective dipole contributing to the depolarizing field, the $\langle\mu(\mathcal{E}_2)\rangle$ moment appearing in Eq. (15) must, in Case E, be replaced by $2zed_1$ (not zed_1) where $2d_1$ is the distance between the charge centroid of the ion and its image. Let $q_a\equiv \theta N_s ze$ be the average adsorbed-layer charge density. Then we may artificially separate the average adsorbent charge density q into an image part, $-q_a$, and a part $(q+q_a)$. If we now apply Gauss' law directly to the situation, considering the charges involved as averaged in the plane but using (15) for $\mathcal{O}_1$ with $\langle\mu(\mathcal{E}_2)\rangle$ replaced by $2zed_1$, we obtain

$$V_1 = 4\pi qd + 4\pi q_a(d - d_1) - 4\pi\mathcal{O}_1 d, \quad (25)$$

from which it follows that

$$\Delta V = 4\pi\theta N_s ze(d - d_1)$$
$$\quad -4\pi\theta N_s[\alpha\{4\pi q + \mathcal{E}_{n1}\} - (\epsilon_{\text{eff}} - 1)(2zed_1)]/\epsilon_{\text{eff}}$$
$$= -4\pi\theta N_s\alpha\{4\pi q + \mathcal{E}_{n1}\}/\epsilon_{\text{eff}}$$
$$\quad -4\pi\theta N_s(zed_1)\{(2/\epsilon_{\text{eff}}) - 1 - (d/d_1)\}. \quad (26)$$

[32] C. A. Barlow, Jr., and J. R. Macdonald "Microscopic Treatment of the Electrolyte Double Layer" (to be published).

[33] J. C. P. Mignolet, Bull. Soc. Roy. Sci. (Liège) 23, 422 (1954).

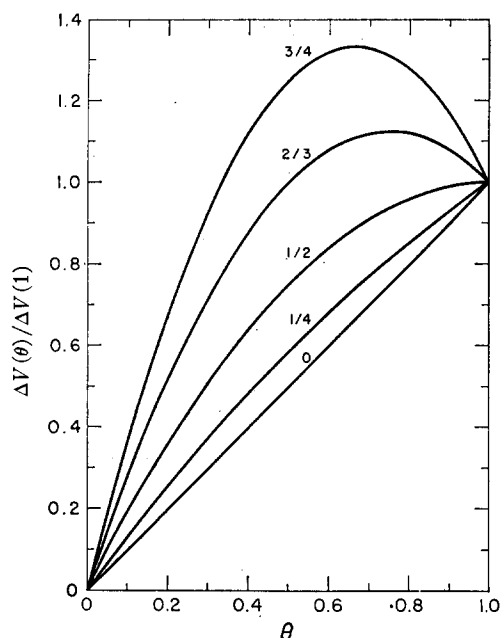FIG. 1. Normalized ΔV vs θ for simplified ionic adsorption [Eq. (31)] for various values of the parameter $A \equiv 4\pi N_s \alpha/d_1$.

This result for ΔV applies when the adsorbent is constrained to have the same surface charge density before and after adsorption and may be pertinent, for example, to the situation of specific adsorption of ions on an electrode from electrolyte solution of variable concentration. Note that when $\alpha = 0$ or when terms involving α are negligible, $\epsilon_{\rm eff} \simeq 1$ and (26) becomes

$$\Delta V = 4\pi\theta N_s\{ze(d-d_1)\}, \qquad (27)$$

and, since $d > d_1$, a positively charged ion leads to a ΔV of sign opposite to that expected from Eq. (1). When adsorption from a gas phase is considered and there is no diffuse charge layer to provide an obvious meaning to "the effective thickness of the adsorbate," as there is in electrolyte adsorption, the quantity d in Eqs. (26) and (27) must be interpreted as the distance over which the potential ΔV is measured, a distance required to be much less than the planar extension of the surface but possibly much greater than the adsorbed layer thickness. In the case considered below, the long-range fields leading to the d dependence above are absent and d does not, therefore, appear.

In most cases of gaseous adsorption or the building up of an adsorbed layer by evaporation, the adsorbent, assumed conducting, will be grounded to a large reservoir of charge and its mean charge density before adsorption may be taken zero. The charge density after adsorption of a layer of ions of charge density q_a will be $q = -q_a$. Then $\Delta V = V_1$ and Eq. (25) predicts

$$\Delta V = -4\pi\theta N_s[\{(\alpha\mathcal{E}_{n1}/\epsilon_{\rm eff}) - zed_1\}$$
$$+ze\{(2d_1/\epsilon_{\rm eff}) - (4\pi\theta N_s\alpha/\epsilon_{\rm eff})\}], \qquad (28)$$

an equation which can show a wide variety of types of

θ dependence when terms involving α cannot be neglected.

In some systems, there seems to be evidence[5,34] that for low θ the adsorbate is laid down as ions but as θ increases subsequent adsorbed elements are atoms. When such variable bonding behavior appears, there may be a range of θ values where both ions and atoms are simultaneously present on the surface. It is then incorrect to analyze the results by means of a combination of the present equations such as the use of (20) with $\theta_1 N_s$ for the atoms, and (28) with $\theta_2 N_s$ ($\theta_1 + \theta_2 \equiv \theta$) for the ions. Such a procedure ignores the cross depolarizing effects of ions on atoms and atoms on ions but may be useful as a first approximation. A less approximate means of treatment has been outlined elsewhere.[24]

Relevant to this same matter, that adsorbate particles may share or give up charge to the adsorbing surface, it is useful to define z as a parameter characteristic not of the adsorbate alone but rather of the complete adsorption system. Thus, if z_n be defined as the valence of the isolated adsorbate entity before adsorption, z and z_n may be unequal, and in fact z may be nonintegral (and may depend on θ). This requires us to consider q to be the mean surface charge density on the adsorbent, related to the charge density in the absence of charge sharing q_n by the equation

$$q = q_n + e(z_n - z)\theta N_s. \qquad (29)$$

With this refinement, the condition that the adsorbing surface is "floating" and that therefore the real average charge density is q, as in Eq. (26), becomes $q_n = q + e(z - z_n)\theta N_s = $ mean charge density before adsorption = constant. Thus, even though the adsorbent "floats" as far as the external circuitry is concerned, a charge density $\theta N_s e(z_n - z)$ is supplied to it by the adsorbate. The condition that the conducting surface is grounded becomes $q = -q_a$, where q_a is still given by $\theta N_s z e$, but where z is now possibly not equal to z_n. We see from the foregoing that the grounded condition may also be written $q_n = -\theta N_s z_n e$, so that the charge density externally supplied to the electrode is the same as before.

When the terms in (28) involving α are negligible, it becomes

$$\Delta V = -4\pi\theta N_s(zed_1), \qquad (30)$$

in agreement with (1) for the image-dipole case, Case D. The several effects of a nonzero α have usually been ignored in comparing theory and experiment. Sometimes,[7,15,35] the presence of α has been recognized by the introduction of a θ-dependent $\epsilon_{\rm eff}$ or ϵ_∞ greater than unity but without the inclusion of other α-dependent terms such as those in (28). In a consistent treatment, these terms must appear and at least some of them will usually be large enough to be of importance. A first approximation to their inclusion has

[34] Reference 6, pp. 123–125.
[35] M. Boudart, J. Am. Chem. Soc. 74, 3556 (1952).

been given by de Boer and Veenemans[5,36] who ignored ϵ_{eff} but included the polarization induced in a single adsorbed ion by its image. This is part of the effect comprised in the $\alpha\mathcal{E}_{nl}$ term of (28), but ϵ_{eff} and the last term on the right of (28), a new and significant contribution, have not been included. In the present self-consistent treatment, the polarizing effect of the image of a given ion is taken into account as well as that of all surrounding ions and their images.

Since α_{ion} is usually of the order of 10^{-24}, the term $\alpha\mathcal{E}_{nl}/\epsilon_{eff}$ in (28) will frequently be negligible compared to the other terms. If further, the difference between ϵ_{eff} and unity is neglected as well, (28) leads to

$$\Delta V(\theta)/\Delta V(1) = \theta(1-\theta A)/(1-A), \qquad (31)$$

where the single parameter $A \equiv 4\pi N_s \alpha/d_1$ does not involve the effective valence z. Figure 1 shows a family of curves plotted from (31). They are of the general form of those deduced from thermionic emission experiments. Furthermore, the existence of a maximum, a general result for metal "ions" on tungsten according to Anderson, Danforth, and Williams,[37] only follows from the theory of Gyftopoulos and Levine[3] when the surface is assumed very rough and the theory does not involve α directly, as it does here.

The theory of Gyftopoulos and Levine[3] predicts only the shape of a ΔV vs θ curve, not the final magnitude $\Delta V(1)$. The present work yields $\Delta V(1)$ as well as shape, provided bonding remains the same over the entire θ range, but is generally inconsistent with the Gyftopoulos–Levine assumption that the work function of a monolayer is independent of the adsorbent and equal to that of the bulk material of the monolayer. Although this question is often confused by uncertainty in experimentally determining the $\theta=1$ point, there seems to be evidence that the above hypothesis is too stringent.[23,37–39] It does not seem likely that a single layer of molecules of one type will shield out all effects from underlying material and exhibit bulk behavior.

It should be clear that the present treatment even for $\theta>1$ will not lead to the final bulk work function of the adsorbate because it treats the adsorbate entities as independent classical elements, disregards collective properties, and thereby ignores the gradual metamorphosis of the adsorbate electron system to a Fermi gas of banded energy structure. Thus, of the several differences between the present work and that of Gyftopoulos and Levine perhaps the most important is that they implicitly assign the principal role to these quantum effects, even though they are introduced phenomenologically.

We do not attempt a detailed fit of (28) or (31) to

TABLE II. Calculations of constants for Cs on W for different surface conditions.

$N_s \times 10^{14}$ (cm^{-2})	$\alpha \times 10^{24}$ (cm^3)	$d_1 \times 10^8$ (cm)	b	A
3.56	2.06	1.58	0.125	0.584
4.89	1.14	1.15	0.109	0.605

ΔV results derived from thermionic emission measurements. First, the present theory deals with a ΔV which is an ordinary average for the surface, while the ΔV obtained from thermionic emission is exponentially weighted toward low work function portions of the surface. A method of surmounting this difficulty, which involves supplementary measurements, is described by Bulyginsky and Dobretsov.[40] Second, as already mentioned, it is unlikely that the adsorbate elements are either solely ions or atoms for the entire θ range. Third, for θ near unity the ideal-dipole approximation used in obtaining ϵ_{eff} may become poor. When this is the case, the expression for ϵ_{eff} may be improved by reducing Λ from 9 somewhat as θ increases. Finally, there is some doubt, especially at appreciable θ, concerning the applicability of the present results because of their aforementioned neglect of the collective, quantum features of the adsorbate elements, effects of uncertain importance for a monolayer and intimately associated with its detailed structure.

In spite of the above limitations, to illustrate the order of magnitude of quantities obtained and the effect of $\epsilon_{eff} \geq 1$, we briefly consider the application of (28) to cesium adsorbed on tungsten. Thermionic emission measurements[11,41] yield approximately -10.1 V for the initial slope $[d(\Delta V)/d\theta]_0$ and -2.6 V for $\Delta V(1)$. Assuming that $\mathcal{E}_{nl} < 10^8$ V/cm so $\alpha\mathcal{E}_{nl}$ may be neglected and taking $z=1$, the above values and (28) lead to the results shown in the last four columns of Table II. The quantity b equals $9\alpha N_s^{\frac{3}{2}}$, so $\epsilon_{eff} = 1 + b\theta^{\frac{3}{2}}$ in the mobile-element case. The first value of N_s given is that expected for a full monolayer of Cs on a perfect [110] surface,[11,41] while the second is that found for the somewhat rough surface usually present.[22] The α values may be compared with the value 2.46×10^{-24} cm^3 given by de Boer[42] for Cs$^+$. The quantity d_1 may be expected to be of the same order of magnitude as the ionic radius, which is 1.67 Å for Cs$^+$. It is gratifying that α and d_1 turn out to be the right order of magnitude and important to note that this only follows for α when the last term in (28) is included.

When the results given in Table II are used in (28) to calculate $\Delta V(\theta)/\Delta V(1)$, the results in the mobile-adsorbate case lie very close indeed to the $A=0.75$ curve of Fig. 1. The effect of $\epsilon_{eff}>1$ is thus here to produce a larger peak than follows from (31) with the same A value, but not to change the shape of

[36] J. H. de Boer and C. F. Veenemans, Physica **1**, 953 (1934).

[37] J. Anderson, W. E. Danforth, and A. J. Williams, III, J. Appl. Phys, "The Adsorption of Thorium on Rhenium" (to be published).

[38] R. C. L. Bosworth and E. K. Rideal, Proc. Roy. Soc. (London) **A162**, 1 (1937).

[39] Reference 2, p. 93.

[40] D. G. Bulyginsky and L. N. Dobretsov, Soviet Phys.—Tech. Phys. **1**, 1115 (1957).

[41] J. B. Taylor and I. Langmuir, Phys. Rev. **44**, 423 (1933).

[42] Reference 5, p. 35.

$\Delta V(\theta)/\Delta V(1)$ vs θ appreciably from that predicted by (31) with a larger A. Note that $\alpha\mathcal{E}_{n1}/zed_1 \simeq 9 \times 10^{-10}\mathcal{E}_{n1}$, when $\mathcal{E}_{n1}$ is expressed in V/cm, for the first row of Table II; thus, the neglect of $\alpha\mathcal{E}_{n1}$ is probably well justified here.

When it is expected that the character of adsorbate bonding changes from ionic to covalent or van der Waals as θ increases, (28) may be used, at least as a first approximation, with α and z taken θ-dependent. If, for example, it is expected that at $\theta = 1$ all the adsorbate entities are atoms, then (28), or (20) with $q = 0$, leads to $\Delta V(1) = -4\pi N_s\alpha_{\text{atom}}\mathcal{E}_{n1}/(1+b)$. Using -2.6 V for $\Delta V(1)$ and $\alpha_{\text{atom}} \simeq 42 \times 10^{-24}$ cm³ for cesium,[42] the assumption $N_s = 4.89 \times 10^{14}$ cm⁻² leads to $b \simeq 4.1$ and $\mathcal{E}_{n1} \simeq 5.1 \times 10^7$ V/cm, a reasonable value. Note, however, that α for an adsorbed atom may not equal that of an isolated atom. The value $\alpha = 20 \times 10^{-24}$ cm³, for example yields $\mathcal{E}_{n1} \simeq 6.2 \times 10^7$ V/cm.

Polarization and ΔV. Permanent and Image Dipoles

Although it is unlikely that an adsorbed entity of interest in electron emission experiments would have both a permanent dipole moment and a nonzero effective valence, this is not the case in some electrolyte double layer situations. In particular, as pointed out to us by R. Parsons, an adsorbed organic ion may have a permanent dipole moment as well. This situation is represented by Case G in Table I, is the most general of our classification, and contains all other situations as special cases.

In order to analyze Case G, we add the terms proportional to $\langle\mu\rangle$ and $2zed_1$ in finding $\mathcal{E}_{\text{eff}}$; we note, on the other hand, that $\langle\mu\rangle$ and zed_1 enter the expression for the potential in an equivalent manner, and we add these contributions. By the arguments presented earlier we obtain

$$\mathcal{E}_{\text{eff}} = [4\pi q - A\delta(\theta N_s)^{\frac{4}{3}}\{\alpha\mathcal{E}_{n1} + 2zed_1 + \langle\mu(\mathcal{E}_2)\rangle\}]/\epsilon_{\text{eff}}. \quad (32)$$

The quantities $\mathcal{E}_{n1}$, $\mathcal{E}_{n2}$, and ϵ_{eff} remain as defined in Eqs. (6), (8), and (14), respectively. For V_1 we may write

$$V_1 = 4\pi qd + 4\pi q_a(d - d_1) - 4\pi\theta N_s\langle\mu(\mathcal{E}_2)\rangle$$
$$- 4\pi\theta N_s\alpha\{\mathcal{E}_{n1} + \mathcal{E}_{\text{eff}}\}, \quad (33)$$

from which it follows that at constant charge density,

$$\Delta V = 4\pi\theta N_s ze(d - d_1) - 4\pi\theta N_s\langle\mu(\mathcal{E}_2)\rangle$$
$$- 4\pi\theta N_s\alpha\{\mathcal{E}_{n1} + \mathcal{E}_{\text{eff}}\}$$
$$= 4\pi\theta N_s ze(d - d_1) - 4\pi\theta N_s\langle\mu(\mathcal{E}_2)\rangle$$
$$- 4\pi\theta N_s\{\alpha\mathcal{E}_{n1} + (4\pi q\alpha/\epsilon_{\text{eff}}) - [(\epsilon_{\text{eff}} - 1)/\epsilon_{\text{eff}}]$$
$$\times[\alpha\mathcal{E}_{n1} + 2zed_1 + \langle\mu(\mathcal{E}_2)\rangle]\}$$
$$= -4\pi\theta N_s\left\{\frac{\alpha(4\pi q + \mathcal{E}_{n1})}{\epsilon_{\text{eff}}}\right.$$
$$\left. + \frac{[2zed_1 + \langle\mu(\mathcal{E}_2)\rangle]}{\epsilon_{\text{eff}}} - ze(d + d_1)\right\}. \quad (34)$$

Note that Eq. (34) goes over into Eq. (26) when $\langle\mu\rangle$ is set to zero.

To obtain the analog to Eq. (28) which holds when $q + q_a$ is fixed at zero we refer to Eq. (33). Since $\Delta V = V_1$ in this case, it follows that

$$\Delta V = -4\pi\theta N_s\left\{zed_1\left(\frac{2}{\epsilon_{\text{eff}}} - 1\right)\right.$$
$$\left. + \frac{\langle\mu(\mathcal{E}_2)\rangle}{\epsilon_{\text{eff}}} + \frac{\alpha}{\epsilon_{\text{eff}}}(\mathcal{E}_{n1} - 4\pi\theta N_s ze)\right\}$$
$$= -4\pi\theta N_s[\{(\alpha\mathcal{E}_{n1}/\epsilon_{\text{eff}}) - zed_1 + (\langle\mu(\mathcal{E}_2)\rangle/\epsilon_{\text{eff}})\}$$
$$+ ze\{(2d_1/\epsilon_{\text{eff}}) - (4\pi\theta N_s\alpha/\epsilon_{\text{eff}})\}]. \quad (35)$$

Again setting $\mu \equiv 0$, Eq. (35) goes over into Eq. (28).

Note that for z and $\mu \neq 0$, there is a contribution $-ze/4d_1^2n^2$ to the natural orienting field $\mathcal{E}_{n2}$ arising from the interaction between the permanent dipole and the image of its accompanying charge. For $z = 1$, $n^2 = 2$, and $d_1 = 2 \times 10^{-8}$ cm, this contribution amounts to a field of about -5×10^7 V/cm. Unless other effects are significant, such a field will line up the dipoles so that $\langle\mu\rangle$ is nearly equal to $-\mu$. This effect may be of considerable importance in the adsorption of thiourea.

The specific adsorption of thiourea[16] on a mercury electrode is qualitatively very similar to that of simple anionic adsorption, such as that of I⁻ in KI solution,[43] while its adsorption behavior is very different from that of aliphatic molecules.[16,17,24] This strongly suggests that z may be nonzero and negative for thiourea molecules adsorbed on mercury. If $z < 0$ for adsorbed thiourea, then there will be a positive term in $\mathcal{E}_2$ from the above imaging effect and an additional positive term from the $2zed_1$ factor in $\mathcal{E}_{\text{eff}}$. These terms together will make $\mathcal{E}_2$ very large and positive, and the thiourea molecule will be adsorbed with the negative pole of its permanent dipole (the sulfur atom end) next to the mercury and the permanent dipole will not be free to rotate. Just such behavior for the permanent dipole appears to be the case.[16,17] The present result, a possible explanation of the apparent pinning and sign of the time-average permanent dipole moment of the adsorbed thiourea molecule, suggests that chemisorption of thiourea on a mercury surface may not be purely by covalent bonding[17] but that the bond may have some ionic character as well[7] which leads to $z < 0$.

Finally, in fitting experiment and theory using any of the more complicated ΔV equations derived herein, it will be found useful to vary adsorbent charge density q where practical. By this means, it may be possible, by analyzing the dependence of ΔV on both θ and q, to determine all unknowns such as $\mathcal{E}_{n1}$, z, d_1, etc., which enter the equation for ΔV.

[43] D. C. Grahame, J. Am. Chem. Soc. **80**, 4201 (1958).