THE
CONTRIBUTION OF POLAR GROUPS TO THE ADHESION
OF
POLYMERS TO CONDUCTING SURFACES

A dissertation submitted to the faculty of the Graduate Department of Applied Science, College of Engineering, University of Cincinnati in partial fulfillment of the requirements

for the degree
of
Doctor of Science
1948
by
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ACKNOWLEDGEMENTS.

The author wishes to express his sincerest appreciation to Dr. Gerard Kraus for recommending this particular problem and for his helpful assistance and criticisms. To Dr. Philip Schwed the author is most thankful for his suggestion in the solution of the quantum mechanical treatment employed in this problem. Last, but not least, the author is indebted to Dr. Walter Soller, the director, for his encouragement and advice regarding the adhesion problem in general.

CONTENTS

INTRODUCTION

The phenomenon of adhesion occurs in all types of phases, i.e., gas-solid, liquid-solid, solid-solid, etc. Even though the general concepts of adhesion forces are well known, the theoretical treatment of any practical system is extremely difficult. Probably for this reason many of the studies reported in the literature[1] have been conducted in an empirical manner. Although, from a practical standpoint, the value of these investigations cannot be denied, very little fundamental information has resulted from this work. When fundamental work was carried out, it was invariably done with simplest systems.[2]

Some investigators[2] have attempted to study adhesion by experimentally observing the properties which are related to it. Contact angle, interfacial tension and wetting are a few of these properties. The direct measurement of adhesion force between two solid materials has been attempted in many instances; however, the methods of measurement employed cannot be considerated adequate.

A great variety of tests for adhesion have been devised, particularly in the laboratories of industrial organizations. The ones most frequently used are the scratch, impact, shear, tensile and peal tests. Although most of these tests were purely empirical, in general, too much emphasis has been placed on the tensile test. When adhesion test specimens are subjected to a load perpendicular to the interface, the stress at that interface is certainly not a pure tensile stress, particularly when the elastic moduli of the two materials vary appreciably. Furthermore, it may be pointed out that tensile testing in general, even on single materials, gives results which cannot be readily interpreted in terms of atomic and molecular forces.

Previous mathematical investigations[3,4,5,6,7], while limited in scope, were concerned with the nature of the intermolecular forces. Most of these investigations deal with the interactions between molecules[8], but some studies have been made on interactions between a molecule of a given substance and a crystal of another[3,7,9]. London and Lennard-Jones[3] were among the first to calculate such interactions with the use of seme-classical and quantum mechanical treatments. Others[6,7,8,9] have continued these investigations along similar lines confining themselves, however, to interactions between neutral gas molecules and metallic surfaces[21]. Although the results of these studies should be directly applicable to the adsorption of gases on metal surfaces, a proper correlation of theory with experimental data appears to be lacking.

No previous attempt has been made to investigate theoretically solid-solid interactions.

SCOPE OF INVESTIGATION

The object of this investigation was to study the effect of polar groups on the adhesion of organic polymers to metal surfaces.

Because of their relative structural simplicity and their practical importance, vinyl type polymers were selected for this investigation.

The dipole moments have been determined on nearly all the vinyl polymers or, at least on the corresponding monomers. The fractionation of vinyl type polymers is relatively simple, and their molecular weights can be readily determined by the viscosity method since the necessary constants for evaluating them have been previously determined by other investigators.

The choice of the vinyl polymers to be used was narrowed to the following: polystyrene, polyvinyl acetate, polyvinyl chloride and polyisoprene. The choice was based upon both theoretical and practical considerations. Theoretically it was desired to obtain a range of magnitude of adhesion , and for practical purposes solubility, ease of fractionation, etc. were considered.

In developing the theory for the adhesion of a polymer to a metallic surface it was assumed that the adhesion results entirely from the interaction between the dipoles of the polymers and the metallic surface. Although this assumption is not strictly true, it is believed that the main contribution to the adhesion is indeed derived from the dipole-image forces. From the results of this theoretical investigation, the theoretical adhesion value for several vinyl polymers was determined by using the known values of the dipole moments.

Experimentally three of the polymers, i.e. polyvinyl chloride, polyvinyl acetate, and polystyrene, were fractionated into a sufficiently large number of fractions and their molecular weights were estimated by the viscosity method. The other polymers had been previously prepared for another project, and were only purified before using. All of the above polymers were prepared for the adhesion test. The test was conducted on an electromagnetic ultracentrifuge. In this test a small quantity of polymer was deposited on a one-quarter inch ball bearing rotor and then the rotor was spun at a speed sufficiently high to separate the polymer from the surface of the rotor. The adhesion force was then calculated. In addition to the electromagnetic ultracentrifuge method of determining the adhesion force, the tensile test method was also used to check order of magnitude agreement.

THEORETICAL TREATMENT

As has been previously stated the adsorption of gases to metals has been treated both classically and quantum mechanically[3,7,9], and the van der Waals relationship between these neutral gas molecules and the metal surfaces have been determined. On the basis of this knowledge, the classical and quantum mechanical treatment of the forces between a solid polymer and a metallic surface was undertaken for this investigation. A number of assumptions applicable to this particular problem had to be made and are discussed at their point of introduction.

(A) Classical Treatment of Adhesion Force between a Polymer and a Metallic Surface.

In this treatment the monomer is the smallest interacting unit considered, i.e. a dipole. Thus the molecule consists of randomly oriented linear dipoles and is on the whole electrically neutral. The metal is regarded as a perfect conductor and the problem becomes essentially one of determining the adhesion force between the randomly oriented dipoles and their images.

In a field of potential U, the potential energy of a dipole is equal to the total work done, against this field, in bringing each charge separately into place. If the potential of a field is U_A for a charge e at A, and U_B for a charge $-e$ at B, then the interaction energy is:

$$V = e\left(U_A - U_B\right) = e\,\overline{AB}\,\frac{\partial U}{\partial S} = \vec{\mu}\,\frac{\partial U}{\partial S}$$

where S is the direction of the dipole axis and $\vec{\mu}$ is the electric moment.

Vectorially then:

$$V = \vec{\mu} \cdot \nabla U$$

The electro static potential due to a dipole is given by:

$$U = \frac{\mu_1 \cos \theta_1}{R^2} = \frac{\vec{\mu}_1 \cdot R}{R^3}$$

The interaction energy between two dipoles of moments μ_1 and μ_2 will be the potential energy of dipole μ_2 in the field of dipole μ_1:

$$V = \vec{\mu}_2 \cdot \nabla\left(\frac{\vec{\mu}_1 \cdot \vec{R}}{R^3}\right) = -\frac{\vec{\mu}_1 \cdot \vec{\mu}_2}{R^3} - \frac{3\vec{\mu}_1 \cdot \vec{R}\,\vec{\mu}_2 \cdot \vec{R}}{R^5} \tag{1}$$

In scalar notation the above equation appears in the well known form of:

$$V = \frac{\vec{\mu}_1 \vec{\mu}_2}{R^3}\left(-2\cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos\varphi\right). \tag{1'}$$

Where θ_1 and θ_2 are the angles of the dipoles with respect to R and φ is angle between the planes of the two dipoles.

In order to use equation (1) for the polymer-metal interaction the following assumptions are made:

(I) Regard the monomers (dipoles) as fixed position but not in orientation. Thus each monomer unit or dipole has a fixed position over which it vibrates.

(II) Consider the distribution of monomer units to be random (Mathematical verification is given in the appendix).

Since the dipole and its image have equal moments and angular difference between the dipole and its image is zero, equation (1) becomes;

$$V_m = -\frac{\mu_m^2 \cos 2\theta}{R^3} + \frac{3\mu_m^2 R^2 \cos^2\theta}{R^5}$$

or

$$V_m = -\frac{U_m^2}{R^3}\left(1 + \cos^2\theta\right) \tag{2}$$

This equation, now represents the interaction between a dipole and its image. In the case of the polymer where there are "n" dipoles and "n" images, the total interaction equation becomes:

$$V_P = -\mu_m^2 \left\{ \sum_{i=1}^{n} \frac{1}{R_i^3}\left(1+\cos^2\theta_i\right) + \sum_{i \neq j}^{n,m} \frac{1}{R_{ij}^3}\left[2\cos\theta_{ij}\cos\theta_{ji} - \sin\theta_{ij}\sin\theta_{ji}\cos(\varphi_{ij}-\varphi_{ji})\right] \right\} \tag{3}$$

Where i represents the dipole and j represents the image of a different dipole.

In examining the second summation term, it can be seen that it may be neglected, since it is assumed that the orientations of the individual dipoles are random with respect to one another, for in that case one obtains a repulsive force as often as an attractive force. This argument was first used by London[14,15] in his discussion of van der Waals forces, both from the standpoint of a static model and from the standpoint of dispersion forces.

The essential features employed in the argument are that if several molecules interact with each other each molecule induces in each of the other a set of co-ordinated periodic dipoles which are in constant phase relation with the corresponding inducing original dipoles. Every molecule then, is the seat of very many incoherently superposed set of induced periodic dipoles caused by different acting molecules. Each of these induced dipoles has always such an orientation that it is attracted by its corresponding generating dipoles, whereas the other dipoles which are not correlated by any phase relation give rise to a periodic interaction only, and on an average over all possible phases contribute nothing to the interaction of energy. Thus, according to London, it is feasible to imagine that simultaneous interaction of many molecules can simply be built up as an additive super-position of single forces[15]. In the case of long chain molecules, London recommends that the attractive forces be built up as a sum of single action of parts of molecules.

Thus on this basis, the total interaction energy of the polymer is the sum of the individual dipole-image interactions. Equation (3) then becomes:

$$V_p = -\mu_m^2 \sum_{i=1}^{n} \frac{1}{R_i^3}\left(1+\cos^2\theta_i\right) \tag{4}$$

According to the Boltzmann Law, the number of dipoles pointing in the direction within a solid angle $d\Omega$ is $Ae^{-V/kT}\,d\Omega$ where A is a constant depending on the number of molecules considered. By integration the total number of molecules in all possible directions is obtained. The total potential energy is $\int AVe^{-V/kT}\,d\Omega$ and the average energy of interaction between a dipole and its image becomes:

$$\overline{V}_m = \frac{-\dfrac{\mu_m^2}{R^3}\displaystyle\int\left(1+\cos^2\theta\right)e^{\frac{\mu_m^2}{kTR^3}\left(1+\cos^2\theta\right)}\,d\Omega}{\displaystyle\int e^{\frac{\mu_m^2}{kTR^3}\left(1+\cos^2\theta\right)}\,d\Omega} \tag{5}$$

substituting:

$$X = \cos\theta$$
$$dx = -\sin\theta\, d\theta$$
$$\lambda(R) = \frac{\mu_m^2}{kTR^3}$$

and simplifying, we have:

$$(6)\quad \overline{V}_m = \frac{-\int \frac{\mu_m^2}{R^3}(1+x^2)\, e^{\lambda(R)x^2}\, dx}{\int e^{\lambda(R)x^2} dx}$$

Integrating and simplifying, equation (6) becomes:

$$(7)\quad \overline{V}_m = -\frac{\mu_m^2}{R^3}\left[1 + \frac{\int_0^1 x^2 e^{\lambda(R)x^2} dx}{\int_0^1 e^{\lambda(R)x^2} dx}\right]$$

and by integrating the quotient of integrals by parts equation (7) reduces to the following form:

$$(8)\quad \overline{V}_m = \frac{\mu_m^2}{R^3}\left[1+\frac{1}{2\lambda(R)}\left(\frac{e^{\lambda(R)}}{\int_0^1 e^{\lambda(R)x^2}dx}-1\right)\right]$$

By differentiating equation (8) with respect to R and letting R = 2r where r represents the distance of the dipole to the metal surface we obtain the adhesion force:

$$(9)\quad \overline{F}_m = \frac{d\overline{V}_m}{dR} = \frac{d\overline{V}_m}{2dr}$$

$\overline{\mathrm{F}}$m represents the average force exerted by each dipole on its image. To obtain the sum of all these forces over an element of unit area we may integrate over all r's, since in a statistical treatment, it is permissible to integrate over a discreet number, because the number of dipoles is sufficiently large to justify the assumption of continuity. Hence, the total adhesion force per unit area becomes:

$$S = \rho\int_a^\infty \frac{d\overline{V}_m}{2dr}dr = \frac{\rho}{2}\int_a^\infty d\overline{V}_m = \frac{\rho}{2}\left[V_m(\infty)-V_m(a)\right]$$

$$(10)\quad S = \frac{\rho\,\mu_m^2}{16a^3}\left[1+\frac{1}{2\lambda(2a)}\left(\frac{e^{\lambda(2a)}}{\int_0 e^{\lambda(2a)x^2}dx}-1\right)\right]$$

Where S is Adhesion Stress and ρ is the Density Factor, $\frac{\sigma N}{M}$

Equation (10) may now be written as follows:

$$S = 3.77 \times 10^{22} \, \frac{u_m^2 \sigma_P}{M_m a^3} \left[1 + \frac{1}{2\lambda(2a)} \left(\frac{e^{\lambda(2a)}}{\int_0^1 e^{\lambda(2a)x^2} dx} - 1 \right) \right] \tag{11}$$

where σ_P = density of polymer
M_m = molecular weight of monomer unit
S = stress in dynes/cm^2
$\lambda(2a) = \frac{u_m^2}{8kTa^3}$

It will be noticed that the dipole moment and molecular weight are that of the monomer, whereas the density is that of the polymer, since a polymer is actually used. Thus, the adhesion force appears to be practically independent of the molecular weight. An alternate treatment which does not assume continuity is given in the appendix. It will be seen that the result is identical.

It should be noted that is is not necessary to use Boltzmann statistics provided that we assume complete randomness of orientation on the part of the dipoles. In fact, this assumption may actually be more valid since the dipoles in a polymer are probably not free to rotate as is the case in a gas. Averaging the interaction energy over all orientation, we obtain:

$$\bar{V}_m = \frac{u_m^2}{R^3} \frac{\int (1+\cos^2\theta)\, d\Omega}{\int d\Omega}$$

$$\bar{V}_m = \frac{u_m^2}{4\pi R^3} \int (1+\cos^2\theta) \sin\theta \, d\theta \, d\varphi$$

which upon integration leads to:

$$(13) \qquad \overline{V}_m = -\frac{4}{3}\frac{\mu_m^2}{R^3}$$

Utilizing this result, we now obtain for S

$$(14) \qquad S = 5.02 \times 10^{22} \frac{\mu_m^2 \sigma_P}{M_m a^3}$$

(B) Quantum Mechanical Treatment of Adhesion Forces between a Polymer and a Metallic Surface.

In this treatment just as in the classical one, the monomer is treated as the smallest interacting unit, and the polymer is considered as made up of randomly oriented linear dipoles. Also the monomer or dipoles are fixed in position and are electrically neutral. The metal is considered as being built up of positive and negative charges.

Consider the interaction between the monomer, with its co-ordinates at the origin, and an element of metal a distance S from the origin. By an element is meant a volume of smaller dimensions than the wave length of radiation corresponding to the predominant resonant frequencies of the molecule, but sufficiently large to possess the properties of the metal[9]. In view of these properties, the total interaction can be obtained by summing up the elements, and the well known equations for polarizability may be employed in solving the problem.

The potential Φ at $\vec{S}$ due to the monomer is:

$$\Phi(\vec{S}) = \frac{e\vec{R}^{(1)}\cdot\vec{S}}{S^3} \tag{1}$$

Where $e\vec{R}$ represents the dipole moment of the monomer and $\vec{R}$ represents the displacement vector, where $\vec{R}^{(1)} = \sum_j \pm \vec{r}_j$ and where $+\vec{r}_j$ represents distance from origin to plus (+) charge and $-\vec{r}_j$ is distance from origin to minus (−) charge.

Since it has been assumed that the metal is made up of positive and negative charges, then it is proper to state, that the element is made up of n positive charges at $\vec{S}_j^{(+)}$ and n negative charges at $\vec{S}_j^{(-)}$ where j = 1, 2, ...

Thus the interaction energy between the metallic element and the monomer will be:

$$V = -e^2 \sum_{j=1}^{n} \frac{\vec{R}^{(1)}\cdot\vec{S}_j^{(+)}}{S_j^{(+)3}} + e^2 \sum_{j=1}^{n} \frac{\vec{R}^{(1)}\cdot\vec{S}_j^{(-)}}{S_j^{(-)3}} \tag{2}$$

Where: $\vec{S}_j^{(+)} = \vec{S} + \vec{r}_j^{(+)}$; $\vec{S}_j^{(-)} = \vec{S} + \vec{r}_j^{(-)}$

If $|r^{\pm}| << S$ then the equation (2) may be expanded and we get for the interaction energy the following:

$$V = e\left[R^{(1)} - \frac{3(\vec{R}^{(1)}\cdot\vec{S})\vec{S}}{S^2}\right]\cdot e\sum_{j=1}^{n} \frac{(\vec{r}_j^{(+)} - \vec{r}_j^{(-)})}{S^3} \tag{3}$$

Since $e\sum(\vec{r}_j^{(2)}-\vec{r}_j^{(1)})$ represents the dipole moment of the metallic element, it may be written $e\vec{R}^{(2)}$, and if vector $\vec{S}$ is taken along the Z axis, the interaction energy may be written in the well known form, as follows:

$$(4)\qquad V=-\frac{e^2}{S^3}\left[X^{(1)}X^{(2)}+Y^{(1)}Y^{(2)}-2Z^{(1)}Z^{(2)}\right]$$

Let: $\psi(1,2)=\psi(1)\,\psi(2)$

represent the unperturbed state function for calculating the interaction energy, where $\psi(1)$ represents the state of the monomer unit and $\psi(2)$ represents the state of the metal, and if the monomer unit is represented as a rigid rotator its wave equation is:

$$\psi(1)=\mathcal{R}(r_1)\,\Phi(\varphi_1)\,\Theta(\theta_1)=\mathcal{R}(r_1)\,P(l_1 m_1;\cos\theta_1)\,e^{im_1\varphi_1}$$

In an unperturbed metal the charge is uniformly distributed to a very high order of approximation which accounts for the fact that there is no permanent dipole moment. Thus the first order expression for the interaction energy vanishes, $\Delta E_1=0$ (see appendix), since it depends upon the product of the dipole moments of monomer and of the metal. The interaction energy is then given by:

$$(5)\qquad \Delta E_2=\sum_b{}'\frac{|V_{ab}|^2}{E_a-E_b}=\sum_{b_1 b_2}\frac{|(l_1 m_1;a_2|V|\lambda_1\mu_1;b_2)|^2}{E(a_1)-E(b_1)+E(a_2)-E(b_2)}$$

where each state b depends upon the quantum number of the monomer (b_1) and metal (b_2).

If equation (5) is averaged over all the magnetic quantum numbers of the monomer, then ΔE_2 becomes:

$$(6)\quad \overline{\Delta E_2} \doteq \frac{1}{2l_1+1} \sum_{m_1} \sum_{\lambda_1 \mu_1 ; b_2} \frac{|(l_1 m_1 ; a_2 | V | \lambda_1 \mu_1 ; b_2)|^2}{E(l_1) - E(\lambda_1) + E(a_2) - E(b_2)}$$

Since the monomer is regarded as a linear rigid dipole and its wave equation is of the form $\psi(1) = \mathcal{R}(r_1)\, \Phi(\varphi_1)\, \Theta(\theta_1)$ the matrix V_{ab} may be expanded and written in spherical co-ordinates, and by these operations the dipole moment of the monomer may be determined:

$$\begin{aligned}(a_1 a_2 | V | b_1 b_2) = {} & (a_1 | eX^{(1)} | b_1)(a_2 | eX^{(2)} | b_2) \\ & + (a_1 | eY^{(1)} | b_1)(a_2 | eY^{(2)} | b_2) \\ & - 2(a_1 | eZ^{(1)} | b_1)(a_2 | eZ^{(2)} | b_2)\end{aligned}$$

Then: $(a_1 | eX^{(1)} | b_1) = e \int \overline{\mathcal{R}}_{a_1} \overline{\Phi}_{a_1} \overline{\Theta}_{a_1} r_1 \sin\theta \cos\varphi\, \mathcal{R}_{b_1} \Phi_{(b_1)} \Theta_{b_1}\, dV$

where $dV = r_1^2 \sin\theta_1\, dr_1\, d\theta_1\, d\varphi_1$ and $\mathcal{R}_{a_1} = \mathcal{R}_{b_1}$ by definition of a rigid rotator, so that now,

$$(7)\quad (a_1 | eX^{(1)} | b_1) = e \int \overline{\mathcal{R}}_{a_1} r_1^3 \mathcal{R}_{a_1}\, dr_1 \int \overline{\Theta}_{a_1} \sin^2\theta\, \Theta_{b_1}\, d\theta \int \overline{\Phi}_{a_1} \cos\varphi_1\, \Phi_{b_1}\, d\varphi_1$$

and similarly for the Y and Z components. The dipole moment of the monomer is now defined as:

$$(8)\quad \mu_m = e \int \overline{\mathcal{R}}_{a_1} r_1^3 \mathcal{R}_{a_1}\, dr_1$$

So now the matrix for V is:

$$(l_1 m_1; a_2 |V| \lambda_1 u_1; b_2) = \Big\{ (l_1 m_1 |\xi| \lambda_1 u_1)(a_2 | e X^{(2)} | b_2) \\ + (l_1 m_1 |\eta| \lambda_1 u_1)(a_2 | e Y^{(2)} | b_2) \\ - 2 (l_1 m_1 |\zeta| \lambda_1 u_1)(a_2 | e Z^{(2)} | b_2) \tag{9}$$

where ξ, η, ζ represent the respective trigonometric functions. Since the molecule is regarded as a rigid dipole and fixed in position only the rotational energy exists, no change in vibrational energy occurring. Generally the rotational energies are small; especially small are the changes in rotational energies of the molecule as compared with the changes in energies within the metal[8,9]. Hence $E(a_2) - E(b_2) \gg E(l_1) - E(\lambda_1)$ so that $E(l_1) - E(\lambda_1)$ may be neglected and $\overline{\Delta E_2}$ becomes:

$$\overline{\Delta E_2} = \frac{1}{2l_1+1} \frac{u_m^2}{S^6} \Bigg[\sum_{m_1} \sum_{\lambda_1 u_1 b_2} \frac{|(l_1 m_1 |\xi| \lambda_1 u_1)(a_2 | e X^{(2)} | b_2) + (l_1 m_1 |\eta| \lambda_1 u_1)(a_2 | e Y^{(2)} | b_2) - 2 (l_1 m_1 |\zeta| \lambda_1 u_1)(a_2 | e Z^{(2)} | b_2)|^2}{E(a_2) - E(b_2)} \Bigg] \tag{10}$$

Upon squaring the terms it is found that the cross-terms drop out, and if the metal is assumed to be isotropic then the equation (10) reduces to:

$$\overline{\Delta E_2} = -\frac{1}{2l_1+1} \frac{u_m^2}{S^6} \Bigg[\sum_{m_1} \sum_{\lambda_1 u_1 b_2} \Big[|(l_1 m_1 |\xi| \lambda_1 u_1)|^2 + |(l_1 m_1 |\eta| \lambda_1 u_1)|^2 + 4|(l_1 m_1 |\zeta| \lambda_1 u_1)|^2 \Big] \sum_{b_2} \frac{|(a_2 | e X^{(2)} | b_2)|^2}{E(b_2) - E(a_2)} \Bigg] \tag{11}$$

Evaluating the matrix, just as was shown by H. Margenau[8], the expression becomes:

$$\overline{\Delta E_2} = -\frac{2}{3} \frac{u_m^2}{S^6} \sum \frac{|(a_2 | e R^{(2)} | b_2)|^2}{E(b_2) - E(a_2)} \tag{12}$$

The polarizability of the metal in quantum mechanical terms is

$$\alpha = \frac{2}{3} \sum \frac{|(a|eR|b)|^2}{E(b) - E(a)}$$ (see appendix)

Thus for the metal where a_2 represents the ground state, the polarizability is:

(13) $$\bar{\alpha}_2 = \frac{2}{3} \sum_{b_2} \frac{|(a_2|eR^{(2)}|b_2)|^2}{E(b_2) - E(a_2)}$$

From this, equation (12) becomes:

(14) $$\overline{\Delta E_2} = -\frac{\mu_m^2}{S^6} \alpha_2$$

Since by definition the static polarizability of a metal is its Volume divided by 2π (appendix) then the average interaction energy for element of metal considered is:

$$\overline{\Delta E_2} = -\frac{\mu_m^2}{2\pi} \frac{dV}{S^6}$$

Therefore the expression for the interaction energy between the monomers and the entire metal becomes upon integration, over infinity in the X and Y direction and from S_0 to ∞ along the Z direction:

(15) $$\overline{\Delta E_2} = -\frac{\mu_m^2}{2\pi} \int_V \frac{dV}{S^6} = -\frac{\mu_m^2}{12 S_0^3}$$

Differentiating equation (15) to obtain the adhesion force between the monomer and metal surface, we have:

(16) $$\overline{F_m} = \frac{\mu_m^2}{4 S_0^4}$$

Proceeding to obtain the total interaction between the metal and the entire polymer, we have as in the case of the classical treatment:

$$S = \frac{\mu_m^2 \rho}{4} \int_a^\infty \frac{dS}{S^4}$$

(17) $$S = \frac{\mu_m^2 \rho}{12 a^3}$$

Where ρ = density factor
a = minimum distance between metal and monomer
S = adhesion force in dynes cm

(18) $$S = 5.02 \times 10^{22} \frac{\mu_m^2 \sigma_P}{M_m a^3}$$

Where σ_P = density of polymer
M_m = molecular weight of monomer unit

Again continuity need not be assumed to obtain the above result. It can be seen that the classical and quantum mechanical results are identical.

In the theory of van der Waals Forces, the expression for the adhesion forces, at large distances of separation is indicated in equations A(11), A(14) and B (18). The short range repulsive forces are still at present, beyond purely theoretical treatment[16,17]. Investigations in the case of simple molecules have been made. It was believed that if the attraction forces are known, available empirical data would fix reasonable limits for the repulsive forces[16,17]. By choosing a repulsive potential which would agree with known values of the second virial coefficient, B, of the equation of state, $PV/RT = 1 + \frac{B}{V} + \cdots$, and by making assumptions suitable to the particular case considered a reasonable degree of success has been obtained for the case of the water molecule and other simple molecules. However, the method is empirical and at best is "an approximation of the truth," although it is to some degree a refinement of the hard sphere (kinetic theory diameter). The particular approach, which uses a refinement of the hard sphere model, does not differ greatly from it. Stockmeyer[18] was able to obtain good agreement with the use of the hard sphere when he neglected quadrupole moments, i.e. considered dipole moments only. From these considerations[16,17,18,19] it appears that the hard sphere model approach is about as satisfactory a method as any at the present time. In addition if one considers the monomers as conducting spheres it can be shown that the radius is equal to the cube root of the polarizability. This has been previously shown to hold to a fair degree of accuracy.

In both classical ~~and~~ quantum mechanical treatment the distance between the interacting elements is presumed to be much larger than the distance between the charges in any individual molecule. Mark[20] points out that an error of 30 percent can be expected when the distance between the reacting elements is only twice that between the centers of charges. However, when the distance is five times, or more, as the distance between charge of the molecule, then the error is only 4 percent. Thus in the latter case, a tolerable accuracy may be expected provided that there are no other forces acting between dipoles, i.e. dispersion forces, quadrupole forces, etc. Since in the treatments in (A) and (B) it is presumed that the predominant forces are dipole forces the criterion for accuracy is applicable.

Consider that the monomer molecule taken as a conducting hard sphere can only approach close enough to contact the metal. The most reasonable assumption as to this distance is that it is the mean distance of closest approach as given van der Waals second virial coefficient. Then the lower limit of integration in both the classical and quantum mechanical treatments is simply the radius of the sphere.

Setting $a^3=\alpha$, the polarizability, the equation for the adhesion force may now be written as follows:

$$S = 5.02 \times 10^{22} \frac{\mu_m^2 \sigma_p}{M_m \alpha}$$

The result obtained classically assuming Boltzmann statistics is:

$$S = 3.77 \times 10^{22} \frac{\mu_m^2 \sigma_p}{M_m \alpha}\left[1 + \frac{1}{2\lambda(\alpha)}\left(\frac{e^{\lambda(\alpha)}}{\int_0^1 e^{\lambda(\alpha)x^2}\,dx} - 1\right)\right]$$

RESULTS AND DISCUSSION

(A) Theoretical Calculations

Equations (A-11) (A-14) and (B-18) were used to calculate adhesion values for a number of different polymers from data in Table I.

Table I

Polymer	Mol. Wt.	Density	Index of Refraction	Dipole moment of monomer unit
Polystyrene(32,35)	104.0	1.0500	1.5900	$.26\times10^{-18}$
Polyvinylacetate(33,35)	86.0	1.2000	1.467	1.71×10^{-18}
Polyvinylchloride(34)	62.5	1.1900	1.5500	1.73×10^{-18}
Polyindene(35)	116.0	1.006	1.5710	$.60\times10^{-18}$
Polyvinylidene-chloride(32,38)	97.0	1.6800	1.600	1.18×10^{-18}
Polyisoprene(39)	68.1	.7160	1.4211	$.10\times10^{-18}$
Polychloroprene(35)	88.5	1.2400	1.5580	1.45×10^{-18}

Table II

POLYMER	ADHESION FORCE		
	Classical		Quantum Mechanical
	Assuming Boltzmann Statistic	Assuming Complete Randomness	Assuming Complete Randomness
olystyrene	$2.58\text{x}10^{6}$ $\frac{\text{dynes}}{\text{sq.cm.}}$ 37.5 $\frac{\text{lbs.}}{\text{sq.in.}}$	$2.56\text{x}10^{6}$ $\frac{\text{dynes}}{\text{sq.cm.}}$ 37.1 $\frac{\text{lbs.}}{\text{sq.in.}}$	$2.56\text{x}10^{6}$ $\frac{\text{dynes}}{\text{sq.cm.}}$ 37.1 $\frac{\text{lbs.}}{\text{sq.in.}}$
olyvinylacetate	$2.80\text{x}10^{8}$ $\frac{\text{dynes}}{\text{sq.cm.}}$ 4050 $\frac{\text{lbs.}}{\text{sq.in.}}$	$2.59\text{x}10^{8}$ $\frac{\text{dynes}}{\text{sq.cm.}}$ 3760 $\frac{\text{lbs.}}{\text{sq.in.}}$	$2.59\text{x}10^{8}$ $\frac{\text{dynes}}{\text{sq.cm.}}$ 3760 $\frac{\text{lbs.}}{\text{sq.in.}}$
olyvinylchloride	$5.00\text{x}10^{8}$ $\frac{\text{dynes}}{\text{sq.cm.}}$ 7230 $\frac{\text{lbs.}}{\text{sq.in.}}$	$4.47\text{x}10^{8}$ $\frac{\text{dynes}}{\text{sq.cm.}}$ 6470 $\frac{\text{lbs.}}{\text{sq.in.}}$	$4.47\text{x}10^{8}$ $\frac{\text{dynes}}{\text{sq.cm.}}$ 6470 $\frac{\text{lbs.}}{\text{sq.in.}}$
olyvinylidene chloride	$1.61\text{x}10^{8}$ $\frac{\text{dynes}}{\text{sq.cm.}}$ 2330 $\frac{\text{lbs.}}{\text{sq.in.}}$	$1.55\text{x}10^{8}$ $\frac{\text{dynes}}{\text{sq.cm.}}$ 2245 $\frac{\text{lbs.}}{\text{sq.in.}}$	$1.55\text{x}10^{8}$ $\frac{\text{dynes}}{\text{sq.cm.}}$ 2245 $\frac{\text{lbs.}}{\text{sq.in.}}$
olychloroprene	$1.20\text{x}10^{8}$ $\frac{\text{dynes}}{\text{sq.cm.}}$ 1740 $\frac{\text{lbs.}}{\text{sq.in.}}$	$1.16\text{x}10^{8}$ $\frac{\text{dynes}}{\text{sq.cm.}}$ 1680 $\frac{\text{lbs.}}{\text{sq.in.}}$	$1.16\text{x}10^{8}$ $\frac{\text{dynes}}{\text{sq.cm.}}$ 1680 $\frac{\text{lbs.}}{\text{sq.in.}}$
olyisoprene	$5.45\text{x}10^{5}$ $\frac{\text{dynes}}{\text{sq.cm.}}$ 7.9 $\frac{\text{lbs.}}{\text{sq.in.}}$	$5.45\text{x}10^{5}$ $\frac{\text{dynes}}{\text{sq.cm.}}$ 7.9 $\frac{\text{lbs.}}{\text{sq.in.}}$	$5.45\text{x}10^{5}$ $\frac{\text{dynes}}{\text{sq.cm.}}$ 7.9 $\frac{\text{lbs.}}{\text{sq.in.}}$
olyindene	$1.04\text{x}10^{7}$ $\frac{\text{dynes}}{\text{sq.cm.}}$ 150 $\frac{\text{lbs.}}{\text{sq. in.}}$	$1.04\text{x}10^{7}$ $\frac{\text{dynes}}{\text{sq.cm.}}$ 150 $\frac{\text{lbs.}}{\text{sq.in.}}$	$1.04\text{x}10^{7}$ $\frac{\text{dynes}}{\text{sq.cm.}}$ 150 $\frac{\text{lbs.}}{\text{sq.in.}}$

It will be observed that the theoretical equations show the adhesion to be practically independent of the degree of polarization, the only variation being that due to the change in density. Furthermore, as a consequence of the basic assumption the adhesion should be independent of the metal as long as the forces remain strictly physical.

(B) Experimental Results

Adhesion values of polystyrene, polyvinylchloride, polyvinylacetate and polyisoprene polymers were determined by the electromagnetic ultracentrifuge method. In order to check for independence of degree of polymerization the above polymers were fractionated and their molecular weights were estimated by the viscosity method.

Unfortunately, the ultracentrifuge in its present design proved to be inadequate in giving adhesion results for polyvinylchloride, polyvinylacetate and polychloroprene since the speed is limited by strength of the rotor and the adhesion of the polymers was found to be in excess of the limits of the machine. For this reason tensile tests on thin films were also run with the objective of obtaining order of magnitude agreement. The results are tabulated in Table III.

Table III

Polymer	Molecular Weight	Adhesion by Ultra-centrifuge method	Adhesion by Tensile Test Method
Polstyrene	unfractionated	14.0 lbs./in.^{2}	12.0 lbs./in^2
	564,000	11.6 " "	10.2 " "
	408,000	14.5 " "	12.7 " "
	302,500	15.7 " "	10.4 " "
	252,000	15.4 " "	11.2 " "
	195,000	15.3 " "	9.0 " "
	158,000	15.5 " "	12.0 " "
Polyvinyl acetate	unfractionated	above 860 lb/in^2	2500 lbs/in^2
	29,600	" " " "	2200 " "
	24,600	" " " "	1800 " "
	18,400	" " " "	2600 " "
	11,800	" " " "	2800 " "
Polyvinyl chloride	unfractionated	above 500 lb/in^2	1280 lb/in^2
	104,000	" " " "	1400 " "
	91,500	" " " "	2080 " "
	36,800	" " " "	1280 " "
	20,700	" " " "	1530 " "
Polyisoprene	unfractionated	3.5 lb/in^2	3.8 lb/in^2

EXPERIMENTAL

The experimental procedure employed in this investigation was divided into five steps:

(1) Fractionation of polyvinyl chloride, polyvinyl acetate and polystyrene.

(2) Molecular weight determination of the above fractionated polymers.

(3) Preparation of fractionated polymers and ball bearing rotors for adhesion test.

(4) Adhesion tests by means of the electromagnetic ultracentrifuge.

(5) Tensile tests on fractionated polymers.

(a) Fractionation of the Polymers

(1) Polystyrene:

Polystyrene was dissolved in methyl ethyl ketone at room temperature at a concentration of 2 percent by weight. Methanol was used as a precipitant to obtain the various fractions. The procedure was identical to that used by Mark, Alfrey, and Bartovies[22]. Polystyrene was obtained through the courtesy of Monsanto Chemical Co.

(2) Polyvinyl Acetate:

Polyvinyl acetate was fractionated by the fractional solution method. It was extracted in a Soxhlet apparatus with butanol. Benzene was used as a solvent and butanol and petroleum ether as precipitants. The procedure was the same as that used by Standinger, Frey and Stark[20,23]. the polyvinyl acetate was obtained through the courtesy of DuPont Chemical Co.

(3) Polyvinyl Chloride:

Polyvinyl chloride was wetted with acetone and then dissolved in cyclohexanone to a concentration of 2.5 percent by weight. With vigorous stirring of the solution while being refluxed, methanol was added very slowly which precipitated out the various fractions. The procedure used was similar to that employed by Fuoss[24]. The polyvinyl chloride was obtained through the courtesy of the B.F. Goodrich Co.

(b) Molecular Weight Determination[25,26,27,28,29,30].

The fractionated polymers were dissolved in the proper solvent, and the intrinsic viscosity of the solution, at a concentration of .25 percent by weight, was determined by means of an Oswald viscosimeter at 30°C.

The following solvents were used:

(a) Toluene for polystyrene fractions.

(b) Benzene for polyvinyl acetate fractions.

(c) Cyclohexanone for polyvinyl chloride fractions.

The determination of viscosity on the various polymer fractions was made with an ordinary Oswald Viscosimeter. Exactly 5 ml. of solution was introduced into the large bulb of the viscosimeter by means of a pipette. The apparatus was suspended in a constant temperature water bath (30°C±.10). After the viscosimeter and solution acquired the temperature of the water bath (approximately 15 minutes) suction was applied at the capillary arm until the level of the solution was above the upper graduation mark. The liquid was then permitted to flow back through the capillary and the time required for the surface of the liquid to pass from the upper to the lower neck was determined with a stop watch.

The following equations were used to determine the intrinsic viscosity and moleculer weight: $[\eta] = \frac{1}{c} \ln \frac{t}{t_o}$

where: t_o = time of solvent
$t_{\circ}$ = time of solution
c = concentration in grams/100 cc.

$$M^a = \frac{[\eta]}{Km}$$

where: $[\eta]$ = intrinsic viscosity
K_m = constant for particular polymer
a = coefficient for a particular polymer
M = molecular weight

The "K_m" and "a" for the polymers used were as follows:

Polystyrene[25]: a = .78
K_m = 5.74×10^{-5}

Polyvinyl acetate[29]: a = 1
K_m = 2.6×10^{-4}

Polyvinyl chloride[28]: a = 1
K_m = 7×10^{-5}

(c) Preparation of Samples for Adhesion Tests:

The ball-bearing rotors were cleaned with acetone to degrease them. After this operation the rotors were immersed in trichloroethylene vapor and kept in it for a period of one hour. Upon drying, the rotors were placed in a vacuum dessicator until they were to be used.

The polymers used in the adhesion tests were dissolved in the proper solvent at a concentration of 40 percent by weight. It was found that the best results were obtained when this concentration was maintained.

By the use of jigs to hold the rotors and a dipper, the rotor was dropped onto a pan, which contained the dissolved polymer. By adjusting the dipper, any size drop could be deposited on the surface of the rotor. With a small amount of experimentation the desired adjustments could be obtained.

After the drops had been deposited on the surface of the rotor, they were permitted to air dry for two hours and then were placed in a vacuum oven and dried at 55-75°C (depending upon the polymer) for 48 hours.

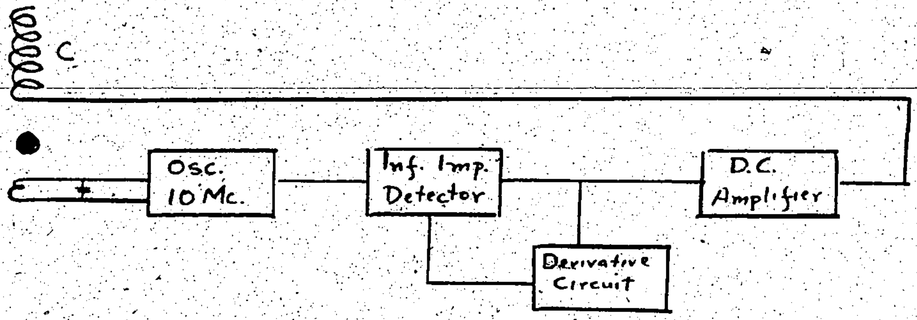
The rotors were weighed on a semi-micro balance to determine the weight of the polymer, and were photographed to determine the area occupied. The samples were then ready for the adhesion test.

(d) The Electromagnetic Ultracentrifuge[31].

The enclosed figure shows a schematic diagram of the electromagnetic ultracentrifuge used in testing the adhesion of polymers to metal. It was developed from the centrifuges used in the production of high centrifugal fields[36]. The rotor spins in a vacuum (10^{-5}mm) which eliminates practically all the air friction forces. The main components used are the supporting circuit, rotating circuit and the measuring circuit.

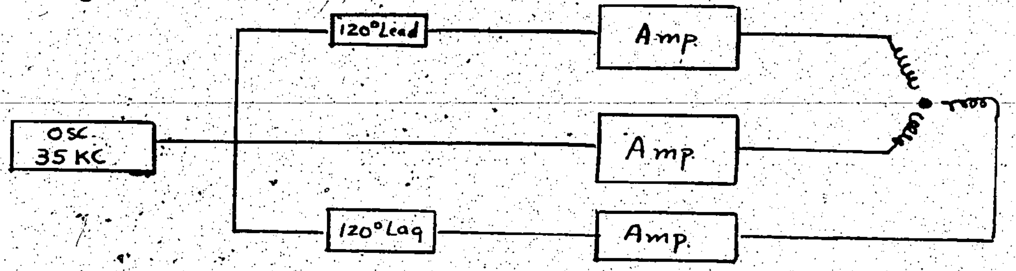
The rotor is supported in the axial magnetic field of the supporting solenoid and is rotated by the rotational field of three coils excited by a three phase oscillator. The horizontal position is determined by the symmetrical field of the supporting solenoid. When the rotor is in equilibrium

Supporting Circuit



Vertical movement of ball is signalled through the coil. The output of the oscillator is varied by the distance of the ball, and is detected by the cathode follower (Inf. Imp, .detector). The amplifier sends the signal to the coil C.

Rotating Circuit:



Measuring Circuit:

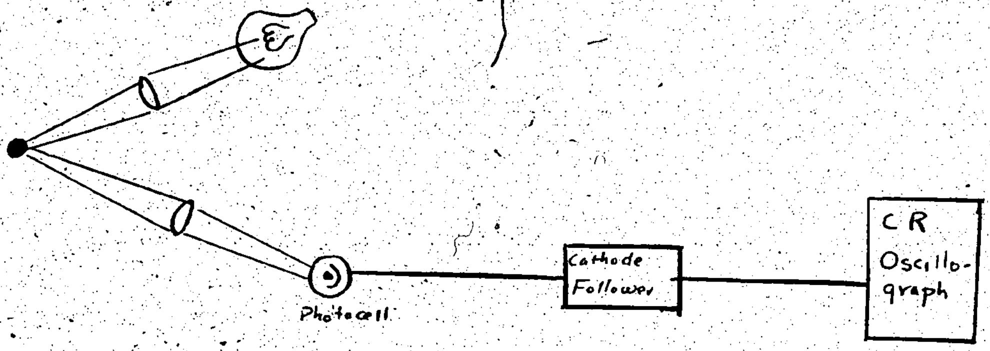


Fig. I Schematic Diagram

position the servo mechanism adjusts the magnetizing current in the supporting solenoid so that it is enough to support the weight of the rotor.

The speed of rotation is determined in the following way: the rotor is illuminated by a light source and a lens focuses the beam of light on the rotor in such a manner as to reflect it into a photocell by transmitting a beam of parallel light to the phototube box. The output of the phototube is fed to an oscilloscope which is calibrated with a standard audio oscillator. The synchronizing frequency of the oscilloscope is the speed of the rotor. The formula for determining the adhesion force is:

$$F = 2.81 \times 10^{-8} \frac{mN^2}{A} \text{ lbs/sq. in.}$$

where m = weight in milligrams

N = speed in rps

A = area of polymer on rotor surface in sq. in.

(e) Tensile Tests

The load necessary to separate a film of polymer from the metal specimen was measured. The specimens used were 1" in diameter and made of hardened steel. The polymer (fractionated and unfractionated) was molded between the two specimens. After cooling, the specimens were removed from the mold. Each specimen was then tested on an Olson Testing Machine.

It was essential throughout this operation (preparation of specimens for tensile test) to insure that the surfaces of the specimen were scrupulously clean, otherwise faulty results were obtained, even when only traces of impurities were present.

SUMMARY AND CONCLUSIONS

Assuming the adhesion of the polymer to a metal to be mainly due to dipole image forces, the adhesion force has been calculated both classically and quantum mechanically for a number of vinyl polymers.

The theoretical treatment leads to the following equations:

Classical:
(Assuming Boltzmann Statistic)

$$S = 3.77 \times 10^{22} \frac{\mu_m^2 \sigma_p}{M_m \alpha} \left[1 + \frac{1}{2\lambda(\alpha)} \left(\frac{e^{\lambda(\alpha)}}{\int_0^1 e^{\lambda(\alpha) x^2} dx} - 1 \right) \right]$$

Quantum Mechanical and Classical:
(Assuming Complete Randomness)

$$S = 5.02 \times 10^{22} \frac{\mu_m^2 \sigma_p}{M_m \alpha}$$

These equations demand that the adhesion force be essentially independent of the degree of polymerization and independent of the metal, as long as the bond is purely physical.

The constancy with molecular weight has been substantiated by experimental results on a set of polystyrene fractions of varying molecular weights. Tensile adhesion tests on other polymers likewise show the same tendency.

The experimental adhesion values obtained by the electromagnetic ultracentrifuge method were found to give good agreement with the theory in the case of polystyrene. Polyvinylchloride and polyvinylacetate were found to be beyond the range of the machine at the present time. The tensile adhesion results, however, show order of magnitude agreement. Furthermore, the tensile results are on the low side of the theoretical values, which should be expected on the basis of the theory of elasticity.

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APPENDIX

Calculation of Minimum Average Distance

Let us now consider the distribution of the monomer through space. If the monomers are assumed to lie in layers then the first layer will extend from a to 3a, the second from 3a to 5a, etc., where a represents the radius of the hard sphere model. This presumes that all the molecules in the first layer cannot touch the surface of the metal. The average minimum distance from the metal surface may then be determined in the following manner:

$$\left\langle \frac{1}{r^4} \right\rangle_{av} = \frac{1}{2a}\left[\int_a^{3a} \frac{1}{r^4}\, dr + \int_{3a}^{5a} \frac{1}{r^4}\, dr + \int_{5a}^{7a} \frac{1}{r^4}\, dr + \cdots\cdots \right]$$

$$\left\langle \frac{1}{r^4} \right\rangle_{av} = \frac{1}{2a}\left\{ \frac{1}{3}\left[\left(-\frac{1}{27a^3} + \frac{1}{a^3} \right) + \left(-\frac{1}{125a^3} + \frac{1}{27a^3} \right) + \cdots \right] \right\}$$

$$\left\langle \frac{1}{r^4} \right\rangle_{av} = \frac{1}{6a^4} \sum_{n=1}^{\infty} \frac{24n^2+2}{(4n^2-1)^3}$$

It will be noticed that $\sum_{n=1}^{\infty} \frac{24n^2+2}{(4n^2-1)^3}$ is very similar to $\sum_{n=1}^{\infty} \frac{1}{n^4} = \frac{\pi^2}{90}$. If the first two terms of the former summation are evaluated then by using the latter summation it will be found that $\sum_{n=1}^{\infty} \frac{24n^2+2}{(4n^2-1)^3} = 1$

Hence:

$$\left\langle \frac{1}{r^4} \right\rangle_{av} = \frac{1}{6a^4}$$

It is now possible to determine the total adhesion force both classically and quantum mechanically and it will be found to be:

Classical: $$F_m = \frac{3\mu_m^2 B}{16r^4}$$

where a = distance between dipole and the metal surface

$$B = \left[1 + \frac{1}{2\lambda}\left(\frac{e^{\lambda}}{\int_0^1 e^{\lambda x^2} dx} - 1 \right) \right]$$

Quantum Mechanical : $F_m = \frac{\mu_m^2}{24a^4}$

where a = distance from center of sphere to metal surface where sphere and metal are in contact with each other.

Now if there are n molecules per layer b cm. thick per square centimeter of surface, then if

$$n' = \frac{\text{molecules}}{\text{cubic centimeters}} = \frac{\sigma N}{M}$$

The number of layers b cm. thick per centimeter of depth equals $1/b$, therefore:

$$n = bn'$$

then:

$$n = \frac{b\sigma N}{M}$$

Since b represents diameter of the sphere, the equation for n may be written as follows:

$$n = \frac{2a\sigma N}{M}$$

or equations become:

$$S = 3.77 \times 10^{2} \frac{\mu_m^2 \sigma_p B}{M_m a^3}$$

$$S = 5.02 \times 10^{22} \frac{\mu_m^2 \sigma_p}{M_m a^3}$$

Mathematical Treatment of Random Orientation of Dipoles

$$\vec{\mu}_m = e(\vec{r}_2 - \vec{r}_1) = e\vec{d}$$

$$\vec{\mu}_p = e\left[(\vec{r}_2 - \vec{r}_1) + (\vec{r}_4 - \vec{r}_3) + - - - - - - - - \right]$$

$$\vec{\mu}_p = e\sum_{j=1}^{n} \pm \vec{r}_j$$

but : $\vec{r}_j - \vec{r}_{j-1} = \vec{d}_i$

now: $\left|\sum_i \vec{d}_i\right|^2 = \sum_i \vec{d}_i \cdot \sum \vec{d}_k$

$$= \sum_{ik} \vec{d}_i \cdot \vec{d}_k$$

However if we have random orientation only the $i=k$ terms will not vanish, hence:

$$\left|\sum_i d_i\right|^2 = \sum_{ik} \vec{d}_i \cdot \vec{d}_k = \sum_{i=1}^{n} \vec{d}_i \cdot \vec{d}_i = nd^2$$

$$\therefore \left|\sum_i d_i\right|^2 = \sqrt{n}\, d$$

Since $\vec{\mu}_p = e\sum d_i$

then $\mu_p = \sqrt{n}\, ed$

but $e\vec{d} = \vec{\mu}_m$

$$\therefore \vec{\mu}_p = \sqrt{n}\, \vec{\mu}_m$$

First Order Perturbation, $\Delta E_1 = 0$

$$V = -\frac{e^2}{S^3}\left(X^{(1)}X^{(2)} + Y^{(1)}Y^{(2)} - 2Z^{(1)}Z^{(2)}\right)$$

$$\Delta E_1 = \int \overline{\psi}_0(1,2)\, V\, \psi_0(1,2)\, d\tau$$

$$\Delta E_1 = -\frac{e^2}{S^3}\int \overline{\psi}_0(2)\,\psi_0(2)\, V\, \overline{\psi}_0(1)\,\psi_0(1)\, d\tau$$

This is permissible because V is a multiplication operator. Substituting for V, ΔE_1, now becomes:

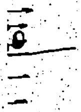
$$\Delta E_1 = -\frac{e^2}{S^3}\left\{ \int \overline{\psi}_0(2)\, X^{(2)}\psi_0(2)\, d\tau \int \overline{\psi}_0(1)\, X^{(1)}\psi_0(1)\, d\tau + \int \overline{\psi}_0(2)\, Y^{(2)}\psi_0(2)\, d\tau \int \overline{\psi}_0(1)\, Y^{(1)}\psi_0(1)\, d\tau - 2\int \overline{\psi}_0(2)\, Z^{(2)}\psi_0(2)\, d\tau \int \overline{\psi}_0(1)\, Z^{(1)}\psi_0(1)\, d\tau \right\}$$

But $X^{(2)} = Y^{(2)} = Z^{(2)} = 0$ because the charge is considered uniformly distributed. Hence:

$$\Delta E_1 = 0$$

Derivation of Polarizability By Means of Quantum Mechanics

The potential energy of dipole in an electric field $\mathcal{E}$ is:



$$H_1 = eR\mathcal{E}\cos\theta$$

Assume dipole in lowest state, $\mathcal{H}(0,b)$; then

$$\psi_0 = \mathcal{R}_0(R)\,C_{00}\,P(0,0\cos\theta)\,e^{i0\varphi}$$

$$\psi_b = \mathcal{R}_k(R)\,C_{\lambda\mu}\,P(\lambda\mu\cos\theta)\,e^{i\mu\varphi}$$

Since:

$$\mathcal{H}_1(0,b) = \int \bar{\Psi}_0\, H_1\, \psi_b\, d\tau$$

$$= \mathcal{E}\int\left[\bar{\mathcal{R}}_0\,\bar{C}_{00}\,\bar{P}(0,0;\cos\theta)\,e^{-i0\varphi}\right] eR\cos\theta\left[\mathcal{R}_k\,C_{\lambda\mu}\,P(\lambda\mu;\cos\theta)\,e^{i\mu\varphi}\right] d\tau$$

Then:

$$\mathcal{H}_1 = \mathcal{E}\left[\int\bar{\mathcal{R}}_0\, eR^3\, \mathcal{R}_k\, dR\right]\left[\bar{C}_{00}\,C_{\lambda\mu}\int_0^{2\pi}\int_0^{\pi}\bar{P}(0,0;\cos\theta)\,\cos\theta\sin\theta\, P(\lambda\mu;\cos\theta)\, e^{i(\mu-0)\varphi}\, d\theta\, d\varphi\right]$$

Now:

$$\mathcal{E}\int\bar{\mathcal{R}}_0\, eR^3\,\mathcal{R}_k\, dR = \mathcal{E}\,(0|eR|b)$$

Thus the above equation for $\mathcal{H}_1$ may now be written as follows:

$$\mathcal{H}_1 = \mathcal{E}\,(0|eR|b)\left[\bar{C}_{00}\,C_{\lambda\mu}\,2\pi\,\delta_{\mu,0}\int\bar{P}(0,0;x)\,x\,P(\lambda\mu;x)\,dx\right]$$

Integrating and simplifying, we have:

$$\mathcal{H}_1(0,b) = (1/3)^{1/2}\,\delta_{\mu,0}\,\delta_{\lambda,1}\,\mathcal{E}\,(0|eR|b)$$

Thus:

$$\mathcal{H}_1(0,0) = \Delta E_1 = 0$$

Obtaining the second order perturbation, we have:

$$\Delta E_2 = \sum_b{}' \frac{|\mathcal{H}_1(0,b)|^2}{E_0 - E_b} = \frac{\mathcal{E}^2}{3} \sum_b \frac{|(0|e\overline{R}|b)|^2 (\delta_{\mu,0})^2 (\delta_{\lambda,1})^2}{E(0) - E(b)}$$

A molecule with polarizability α will have a change in energy, and classically it is expressed in the following manner:

$$\Delta E_2 = -\tfrac{1}{2} \alpha \mathcal{E}^2$$

$$\therefore \quad \alpha = \tfrac{2}{3} \sum_b \frac{|(0|e\overline{R}|b)|^2}{E(b) - E(0)}$$

Static Polarizability of a Metal

By definition the static polarizability is the volume of the metal divided by 2π. This may be shown to be so in the following manner:

$$\sigma = \frac{E}{2\pi}$$

where σ = surface charge density

E = electric field

If the above equation is multiplied through by the volume, we have:

$$\sigma A d = \frac{EV}{2\pi}$$

where V = volume of metal slab

A = area of metal slab

d = thickness of metal slab

but σAd = dipole moment, μ

Then $\dfrac{\mu}{E} = \dfrac{V}{2\pi}$

When E = unity, then $\dfrac{\mu}{E} = \alpha$

$$\therefore \quad \alpha = \frac{V}{2\pi}$$