

intensity (about  $10^{12}$  quanta/cm.<sup>2</sup>/sec.) simple expressions of the type

$$\frac{R_{\text{benzene}}}{R_{\text{diphenyl}}^{1/2}} = \frac{k_1[\text{RH}]}{k_2^{1/2}} \times f(\epsilon, c, L)$$

are obtained,<sup>6</sup> where  $c$  is the source concentration and  $L$  is the path length; approximating our 10 cm. spherical vessel to a cylinder of  $L = 7$  cm., these functions  $f(\epsilon, c, L)$  come out to 2.6 and 2.3, respectively, for the limiting cases. The important point is that this modifying function is independent of temperature (provided  $\epsilon$  and the quantum yield of the primary photolytic step, which we assume is always 2, are both temperature independent), and therefore the activation energy differences which we measure will be correct.

### Results

Kinetic experiments were carried out over the range 180–350°; it is inconvenient to go much outside this range because of the low volatility of mercury diphenyl below 180°, and because of the onset of thermal decomposition of mercury diphenyl above 350°. Photolyses were carried out for the shortest time which would give sufficient products for analysis (about 15 min. with  $I_0 \approx 10^{14}$ – $10^{15}$  quanta/cm.<sup>2</sup>/sec. at 2357 Å.). The results are shown in Fig. 1 and the derived activation energies and *apparent*  $A$ -factors are given in Table I; it is not possible to quote absolute values for  $A_1/A_2^{1/2}$  because the analysis given in the preceding section is complicated by the build-up during the photolysis of diphenyl which absorbs strongly at 2537 Å. No correction was made for the attack of phenyl radicals on the mercury diphenyl source because separate experiments showed that this would be negligible under our experimental conditions.

### Discussion

No abstraction reactions of phenyl radicals have been measured previously, and our observations show that their activation energies are lower than the corresponding reactions of other free radicals, assuming that  $E_2 \approx$  zero. The  $A$ -factor ratios, although uncorrected, are clearly of the correct order of magnitude.

Using our data on methane and fluorofrom, we are now in a position to make two estimates for

TABLE I<sup>a,b</sup>

ARRHENIUS FACTORS FOR THE REACTION  $\text{Ph} + \text{RH} \rightarrow \text{PhH} + \text{R}$

RH	$k_1/k_2^{1/2}$ (apparent)	$E_1 - \frac{1}{2}E_2$ (kcal./mole)	$A_1/A_2^{1/2}$
	at 182° (molecule <sup>-1/2</sup> cm. <sup>3/2</sup> sec. <sup>-1/2</sup> )		(apparent) (molecule <sup>-1/2</sup> cm. <sup>3/2</sup> sec. <sup>-1/2</sup> )
H <sub>2</sub>	$9.4 \times 10^{-12}$	$6.5 \pm 1$	$1.2 \times 10^{-8}$
CH <sub>4</sub>	$5.2 \times 10^{-12}$	$7.5 \pm 0.5$	$2.0 \times 10^{-8}$
CF <sub>3</sub> H	$6.2 \times 10^{-12}$	$5.2 \pm 0.5$	$1.9 \times 10^{-9}$

<sup>a</sup> For convenience of comparison with other radical data, approximate rate-constant ratios are quoted at 182° although this temperature is just at the limit of our range. <sup>b</sup> The last two columns in this table represent the equations of the lines drawn in Fig. 1. These lines were drawn by eye and the error limits quoted represent the largest reasonable amount by which we feel they may be skewed. In the particular case of H<sub>2</sub>, the three points at  $10^3/T \approx 1.9$  have been given less weight than the others because the photolysis time for these particular points was too long, and they are certainly somewhat low on this account.

$D(\text{Ph-H})$  by comparing reactions 1 and 3, and 1' and 3'. Assuming that all the recombination reactions have zero activation energy (*i.e.*, methyl, trifluoromethyl, and phenyl) we have

$$\begin{aligned} D(\text{Ph-H}) &= D(\text{CH}_3\text{-H}) + E_3 - E_1 \\ &= 102.5 \pm 1 + 9.2 \pm 0.2 - 7.5 \pm 0.5 = 104.2 \pm 1.7 \text{ kcal./mole} \end{aligned}$$

and

$$\begin{aligned} D(\text{Ph-H}) &= D(\text{CF}_3\text{-H}) + E_3' - E_1' \\ &= 102.0 \pm 2 + 6.3 \pm 0.2 - 5.2 \pm 0.5 = 103.1 \pm 2.7 \text{ kcal./mole.} \end{aligned}$$

These two determinations would be independent except for the fact that  $D(\text{CF}_3\text{-H})$  is at present directly related to  $D(\text{CH}_3\text{-H})$ .<sup>11,14</sup>

Finally, consideration of our results for hydrogen gives additional confirmation of the essential correctness of these values: the activation energy for the attack of H atoms on benzene<sup>15</sup> is  $E < 7$  kcal., which, taken in conjunction with our results gives  $D(\text{Ph-H}) < 104.5$  kcal./mole.

(14) We have used  $D(\text{CH}_3\text{-H}) = 102.5 \pm 1$  to be consistent with earlier work<sup>11</sup> but recent measurements by G. C. Fettes and A. F. Trotman-Dickenson [*J. Chem. Soc.*, 3037 (1961)] suggest that this might need raising a little.

(15) H. I. Schiff and E. W. R. Steacie, *Can. J. Chem.*, **29**, 1 (1951).

## ON THE ADSORPTION OF POLYELECTROLYTES AT PLANAR DIELECTRIC SUBSTRATES

BY H. L. FRISCH AND F. H. STILLINGER

*Bell Telephone Laboratories, Inc., Murray Hill, New Jersey*

Received September 11, 1961

We have examined the effect of charges on polyelectrolytes on the adsorption free energy at a dielectric interface. We restrict ourselves initially to summing over all charges the electrical image forces, and then estimate separately the non-electrostatic contributions to the free energy. We discuss the effect of  $pH$  changes and added electrolyte on the adsorption isotherm.

### 1. Introduction

A number of experimental investigations of the adsorption of natural<sup>1</sup> and synthetic<sup>2-4</sup> polyelec-

(1) A. D. McLaren, *J. Phys. Chem.*, **58**, 129 (1954); A. D. McLaren, G. H. Peterson, and I. Barshad, *Soil. Sci. Soc. Amer. Proc.*, **22** (1958).  
(2) T. L. Pugh and W. Heller, *J. Polymer Sci.*, **47**, 219 (1960).

trolytes have been carried out recently or are under way. It therefore appears desirable to extend the theory of polymer adsorption,<sup>5</sup> particularly at the

(3) I. R. Miller, *Trans. Faraday Soc.*, **57**, 301 (1961); I. R. Miller and D. C. Grahame, *J. Colloid Sci.*, **16**, 23 (1961).

(4) R. J. Lauria, W. Schmidt, and F. R. Eirich, to be published.

solid-liquid interface, to the case of electrically charged macromolecules and/or solid adsorbents carrying electrical charges. A number of formidable problems arise in attempting to do this which become especially severe as the polymer concentration in the bulk solution, in contact with the solid adsorbent, increases. In view of this we shall in our theory be almost exclusively concerned with the most dilute concentration region in which the expected electrical potentials surrounding the macroion in bulk and at the interface are adequately described by appropriate solutions of the linearized Poisson-Boltzmann equation. A second consequence of considering only very dilute macroion solutions is that the adsorption isotherm relating the surface concentration  $c_s$  to the bulk macroion concentration  $c$  will be linear<sup>5</sup>

$$c_s = Kc + O(c^2) \quad (1.1)$$

$$\left(\frac{\partial c_s}{\partial c}\right)_{c \rightarrow 0} = K$$

where  $K$  is a constant sometimes called the affinity.<sup>4</sup> This relationship is in many ways analogous to an interfacial Henry's law. We wish to compute  $K$ .

A further difficulty encountered with polyelectrolytes is their ability in some instances to modify their shape and dimension drastically with changes in their electrical environment. Thus an essentially randomly coiled polyion can for instance straighten out into an effectively rod-like or cigar-like shape on being brought from the bulk solution to the immediate vicinity of the adsorbent surface. This change in shape furthermore can affect the electrical environment as well as modify the adsorption behavior of the macroion. In this paper we restrict ourselves for simplicity to a model polyion which is a long rigid rod structure along which point charges  $Ze$  are distributed at random. There are  $N\alpha$  such charges where  $N$  is the total number of ionizable groups and  $\alpha$  represents the fraction ionized in solution. We assume that  $\alpha$  is the same on the surface although clearly at high degrees of surface coverage by macro- or microions this cannot strictly be the case. Our  $\alpha$  thus is essentially to be obtained from the bulk titration curve. Reasoning only by analogy to the adsorption behavior of uncharged polymers,<sup>5</sup> we expect that this simple model may at least qualitatively reproduce the adsorption behavior of real polyelectrolytes (even when their shapes depart from a rod-like structure) if the effective parameters of the rod-like model are suitably interpreted. The next section will be devoted to the affinity calculation for a rigid rod-like polycation or polyanion and the modification of these results for the case of a polyampholyte.

As the concentration of the bulk polyelectrolyte solution increases one expects to observe saturation of the adsorbent, merely because of the depletion of free surface sites and the small tendency even uncharged polymers show for extensive multilayer formation. The description of the shape and the capacity<sup>4</sup> of the complete adsorption isotherm is beyond the limits of the theory we shall develop. Nevertheless we shall make certain qualitative ob-

servations concerning these characteristics in a subsequent section. In the last section we shall make some comparisons of the theory with available experimental information. In part, the value of even such a simplified model theory as the one we shall develop is to indicate clearly the necessity for studying experimentally the affinity and capacity as well as the zeta potential of the pure adsorbent in the given solvent as a function of pH, temperature, etc., at constant ionic strength.

**2. The Affinity.**—We assume that our rigid rod polycation or polyanion solution is essentially so dilute as to be ideal, except for effects due to the ion atmospheres around the ionized groups on the polymer. To compute the free energy change on adsorption of our macroion we shall: (1) initially discharge the designated macroion in the bulk of solution; (2) bring the uncharged rod to the immediate vicinity of the adsorbent surface (which we take to be planar), arranged so as to assume the most probable final orientation which turns out to be parallel to the surface; and (3) finally recharge the rod so as to attain a random distribution of  $N\alpha$  ionized groups along its length.

We refer chemical potentials to the ideal, bulk solution of uncharged rods, for which we can write

$$\mu = \mu^{(0)}(T) + kT \ln c \quad (2.1)$$

Similarly on the surface, the chemical potential of these uncharged rods can be written

$$\mu = \mu_s^{(0)}(T) + kT \ln c_s \quad (2.2)$$

If the rods remain uncharged, the condition for equilibrium which is the equality of  $\mu$  as given by (2.1) and (2.2) yields immediately the linear relation

$$c_s = \exp \left[ \frac{\mu^{(0)}(T) - \mu_s^{(0)}(T)}{kT} \right] c \quad (2.3)$$

Comparing (2.3) with (1.1) we see that for the un-ionized rods the affinity is, as expected, independent of ionic strength, pH, as well as the surface charge  $\sigma$  on the adsorbent, if any. If the rod now is allowed to ionize, the affinity  $K$  will involve an additional electrical adsorption free energy  $W$  and (2.3) becomes

$$\frac{c_s}{c} = K = \exp \left[ \frac{\mu^{(0)}(T) - \mu_s^{(0)}(T) - W}{kT} \right] \quad (2.4)$$

where  $W$  may be interpreted as the reversible electric work that must be done in bringing the charged rod up to the surface. This work can be written as a product of the charge on the rod times one-half the change in mean electrostatic potential (caused by bringing the rod up to the surface) measured at the position of a typical ionized group on the linear macromolecule.

Fortunately, Stillinger<sup>6</sup> previously has considered in sufficient detail the appropriate solutions for this mean potential of the linearized Poisson-Boltzmann equation for boundary conditions corresponding to fixed point charge ions near the planar boundary between an electrolyte solution and a dielectric substrate. In what follows we shall pursue closely the basic theory developed in reference 6 which incidentally sketches the implications for simple (micro) ionic adsorption processes. Our

(5) H. L. Frisch and R. Simha, *J. Chem. Phys.*, **24**, 652 (1956).

(6) F. H. Stillinger, Jr., *Ibid.*, **35**, 1584 (1961).

model rod within the framework of this theory corresponds to a rigid linear distribution of monomer units which may ionize to yield point charges along the rod's axis. Using essentially eq. 20 of reference 6 adapted for our model, one finds that the mean potential is highly peaked in favor of a parallel orientation of the rod to the planar substrate. Adapting immediately this orientation, with only negligible error, one finds that  $W$  can be written as a sum of 4 contributions. Only the last of these involves the surface charge density  $\sigma$  of the substrate.

The first contribution to  $W$  is the unshielded image work per ionized group which amounts for  $N\alpha$  groups to

$$N\alpha W \quad (2.5)$$

where  $w$  is the shift in adsorption free energy,  $A$ , for a monomer unit in pure solvent, caused by ionization, *i.e.*,

$$w = A_{\text{ionized}} - A_{\text{un-ionized}} \quad (2.6)$$

We are particularly interested in the dielectric constant dependence of  $w$ . Denoting by  $D$  and  $D_s$  the dielectric constants of the solution and adsorbent, respectively, we expect  $w$  to be positive if  $D_s < D$  and negative if  $D_s > D$ . This contribution amounts to the work which has to be done in bringing an unshielded ionized group against the potential due to the single image charge within the surface, to an effective distance  $l$ . This distance,  $l$ , which is a characteristic of the adsorption system, is essentially determined by the molecular attractive surface forces responsible for the adsorption as well as the finite size of the adsorbing monomer units. With this characteristic cutoff distance  $l$  we can formally write for  $w$

$$w = \frac{D - D_s}{D + D_s} \times \frac{(Ze)^2}{4\pi D l} \quad (2.7)$$

as would be expected from simple electrostatic theory (Poisson's equation).

The second contribution to  $W$  is the atmosphere displacement work, equal to (*cf.* eq. 24 of ref. 6)

$$\frac{N\alpha(Ze)^2\kappa}{D} F(\gamma) \quad (2.8)$$

where  $\kappa$  is the Debye shielding parameter,<sup>7</sup> which depends on the ionic strength,  $\gamma$  is  $D/(D + D_s)$  and

$$F(\gamma) = 1/2 - \gamma^2 \int_0^\infty dl \frac{[(1 + l^2)^{1/2} - l]}{\gamma[(1 + l^2)^{1/2} - l] + l} \quad (2.9)$$

The function  $F(\gamma)$  is plotted *vs.*  $\gamma$  in Fig. 2 of ref. 6, while for very small  $\gamma$ ,  $F(\gamma) \cong \gamma^2 \ln \gamma + 1/2$ . This contribution represents the reversible work required to displace the ion atmospheres surrounding the ionized groups into one hemisphere as each of these charges is brought up to the interface from the bulk solution.

The third contribution to  $W$  which must be considered arises because of the change in the shielded interaction, between surface and bulk, for pairs of ionized groups along the rod. If the rod is sufficiently long<sup>8</sup> so that end effects can be neglected

(7) This Debye  $\kappa$  refers only to small ions.

(8) Strictly speaking in the limit as the length of the rod and  $N$  approach infinity in such a way that average charge density on the rod remains constant.

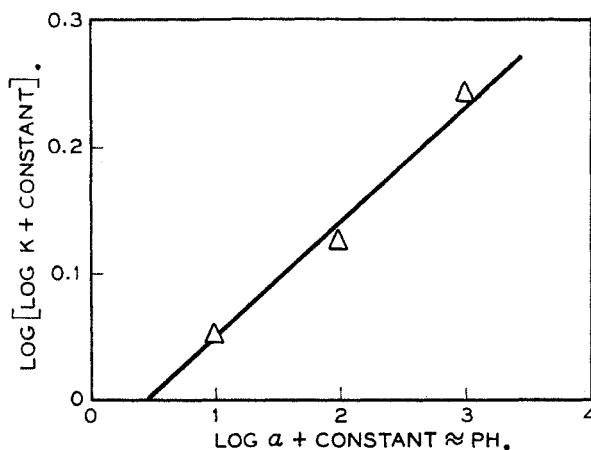


Fig. 1.—Plot of  $\log [\log (10^6 K)]$  *vs.*  $\log \alpha + \text{constant} \approx pH$  for aqueous polyacrylic acid ( $M = 6 \times 10^5$ ) adsorbed on anatase ( $\text{TiO}_2$ ) at a constant ionic strength of 0.1 at 25°. ( $K$  is dimensionless, being expressed as grams of polymer adsorbed per gram of adsorbent divided by grams of polymer per gram of polymer solution.)

and the average distance between neighboring randomly distributed ionized groups is  $a$  we can set this contribution equal to

$$\frac{N\alpha^2(Ze)^2\kappa}{D} \sum_{j=1}^{\infty} \int_0^\infty dl J_0(\kappa ja) l \left\{ \frac{2\gamma}{\gamma[(1 + l^2)^{1/2} - l] + l} - \frac{1}{(1 + l^2)^{1/2}} \right\} \quad (2.10)$$

with  $J_0(x)$  the zeroth order Bessel function of the first kind of  $x$ , by virtue essentially of eq. 25, etc., of ref. 6, applied once for the mean surface potential and once for the mean bulk potential. When  $\gamma \neq 1$ , the dominant small  $\kappa$  behavior is rigorously obtained from (2.10) by replacing, in the integrand,  $2\gamma/\{\gamma[(1 + l^2)^{1/2} - l] + l\}$  by  $2\gamma/(1 + l^2)^{1/2}$ . Equation 2.10 then simplifies to

$$\frac{N\alpha^2(Ze)^2\kappa}{D} \left( \frac{D - D_s}{D + D_s} \right) \sum_{j=1}^{\infty} \frac{e^{-\kappa ja}}{\kappa ja} = - \frac{N\alpha^2(Ze)^2\kappa}{D} \left( \frac{D - D_s}{D + D_s} \right) \frac{1}{\kappa a} \ln(1 - e^{-\kappa a}) \quad (2.11)$$

As can be seen from (2.11) the change of interaction between pairs of ionized groups along the rod can in this limiting case be calculated as if the ion atmosphere of one group acted independently of the other. Even for larger  $\kappa$ , the integrand simplification of (2.10) still gives qualitatively the correct behavior. For very large  $\kappa$  this effect is completely negligible as can be seen directly from (2.10).

The final contribution to  $W$  is the work of bringing the charged rod up to the adsorbent surface, which itself bears a uniform surface charge density  $\sigma$ .<sup>9</sup> The zeta potential  $\zeta$  for such a surface, computed from the appropriate solution of the linearized Poisson-Boltzmann equation is just

$$\zeta = \frac{4\pi\sigma}{\kappa D} \quad (2.12)$$

The corresponding reversible work for bringing up the charged rod is

$$N\alpha Ze\zeta = \frac{4\pi N\alpha Ze\sigma}{\kappa D} \quad (2.13)$$

(9) In the  $c \rightarrow 0$  limit,  $\sigma$  is due only to small ions.

Combining (2.5), (2.7), (2.8), (2.11), and (2.13) we find that

$$W = \frac{N\alpha(Ze)^2}{D} \left\{ \frac{1}{4l} \left( \frac{D - D_s}{D + D_s} \right) + F(\gamma)\kappa - \alpha \left( \frac{D - D_s}{D + D_s} \right) \frac{1}{a} \ln(1 - e^{-\kappa a}) + \frac{4\pi\sigma}{\kappa Z e} \right\} \quad (2.14)$$

and using (2.4)

$$\ln K = \ln K_{\text{un-ionized}} - \frac{W}{kT} \quad (2.15)$$

with

$$K_{\text{un-ionized}} = \exp \left\{ \frac{\mu^{(0)}(T) - \mu^{(0)}(T)}{kT} \right\} \quad (2.16)$$

of (2.3).

The pH dependence of eq. 2.15, at constant ionic strength, resides completely in the pH dependence of  $\alpha$  and  $\sigma$ , which we presume to be given functions of the pH. For vanishingly small  $\kappa$ , the second and third terms on the right-hand side of (2.14) can be neglected in comparison with the first and fourth terms. In this case, if  $\sigma$  furthermore is constant with changes in pH, at constant  $\kappa$ , we see that the pH dependence of  $\ln K$  is directly proportional to the pH dependence of  $\alpha$ . The importance of the dielectric constant immediately is apparent from (2.15). Given two polyelectrolytes, their adsorption behavior from solution onto a given substrate, if their electrical properties and environments are the same, is essentially determined by  $K_{\text{un-ionized}}$ . Then the affinity is the larger the smaller the solubility of the polymer in the given solvent.

To extend the previously developed theory of the affinity of polycations or polyanions to polyampholytes, we recognize that the generalization required is notational rather than conceptual. Thus, in place of a single charged state  $Ze$  previously available per monomer unit, it is necessary generally to admit states  $Z_1e, Z_2e, \dots, Z_n e$ , representing, respectively,  $N\alpha_1, N\alpha_2, \dots, N\alpha_n$  point charges along the axis of the rod-like macromolecule.<sup>10</sup> For evaluation of the modified electrostatic contribution  $W$  to the affinity  $K$ , (2.9), we exhibit each of the four contributions previously discussed is the simpler case. Analogous to the previous presumption, the quantities  $\alpha_1, \dots, \alpha_n$  will be treated as experimentally available from bulk solution properties such as the titration curve.

The unshielded image work obviously becomes

$$\sum_{i=1}^n N\alpha_i w_i, \quad w_i = \frac{D - D_s}{D + D_s} \times \frac{(Z_i e)^2}{4Dl_i} \quad (2.17)$$

One should of course be prepared to admit the necessity of distinct length parameters  $l_i$  for each monomer unit charge state; nevertheless it probably is true that these quantities do not differ drastically from one another, being equal to one or two Ångström units, unless the ionizing monomer units undergo radical steric changes with change in charge state.

The atmosphere displacement work, like the unshielded image work (2.17), is additive for all mono-

(10) For most polyampholytes, of course,  $n = 2$  and  $Z_1$  and  $Z_2$  are just  $+1$  and  $-1$ . The more general scheme here includes the possibility of monomer units being themselves, for example, polybasic acids.

mer units; its generalization is

$$\sum_{i=1}^n \frac{N\alpha_i(Z_i e)^2 \kappa}{D} F(\gamma) \quad (2.18)$$

That contribution to  $W$  arising from the change in shielded interaction between ionized monomer units, in passing from bulk to interface, can depend upon the mean distribution of units along the rod (e.g., atactic or isotactic distribution of acidic and basic monomers). For simplicity, we suppose that the various charge states of the monomers are randomly placed along the rod. The corresponding analog of expression (2.11) is

$$- \frac{N\kappa}{D} \left[ \sum_{i=1}^n \alpha_i(Z_i e) \right]^2 \left( \frac{D - D_s}{D + D_s} \right) \frac{1}{\kappa a} \ln(1 - e^{-\kappa a}) \quad (2.19)$$

Finally, electrostatic work of polyampholyte adsorption against the (adsorbed microion) surface charge  $\sigma$  mean potential, the  $\zeta$  potential has the form

$$\frac{4\pi N\sigma}{\kappa D} \sum_{i=1}^n \alpha_i(Z_i e) \quad (2.20)$$

The sum of the four expressions (2.17)–(2.20) is the appropriate polyampholyte  $W$ , which, when inserted into (2.9), yields the affinity  $K$ .

**3. Qualitative Considerations Concerning the Isotherm and the Capacity.**—Although mathematical difficulties preclude a quantitative theory of the complete adsorption isotherm we can make certain speculations concerning the shape of the isotherm on the basis of our knowledge of the adsorption behavior of non-ionic polymers. In more concentrated solutions the affinity calculated in the previous section no longer acts as the adsorption equilibrium constant. This is due to a number of effects, e.g.: (1) The effect due to the non-ideality of the solution which introduces activity corrections, which arise because in more concentrated solutions the concentrations in (2.1) and (2.2) have to be replaced by the corresponding activities. (2) The reversible electrical work  $W$  has to be replaced by  $W(\theta)$ , the modified reversible work of bringing up an ionized macroion to a surface of which a fraction  $\theta$  of the sites already are occupied by previously deposited polymer segments. (3) The effects due to, in general, non-athermal lateral interactions between deposited polymer molecules. For small  $\theta$  we can, by virtue of the known limiting behavior, write for the equilibrium adsorption coefficient  $K_{\text{is}}(\theta)$

$$K_{\text{is}}(\theta) = K(1 + 0(\theta)) \quad (3.1)$$

with  $K$  the previously calculated affinity.<sup>11</sup>

The shape of the isotherm also will strongly depend on the extent of deposition of the segments of the adsorbed polyelectrolyte. In the presence of sufficiently strong attractive electrical forces between the substrate and the adsorbed macromolecule the fraction  $p$  of segments anchored at the adsorbent surface can be an appreciable fraction of the total number of segments.<sup>5</sup> A theory of this factor has been given<sup>12</sup> and a more refined version was

(11) By  $0(\theta)$  as  $\theta \rightarrow 0$  we mean a function of  $\theta$  which approaches zero faster than  $\theta$ .

developed by Higuchi.<sup>13</sup> This indeed is experimentally found to be the case for both ionized and un-ionized aqueous polyvinylpyridine, polymethacrylic acid, and polyacrylic acid at a mercury surface.<sup>3</sup> Thus the number of anchor segments  $\nu$  will be of the order of the total number of segments. An immediate consequence of this will be found in the great difficulty of completely reversibly removing deposited polymer with the same solvent, etc. At constant ionic strength and surface charge  $\sigma$  a change in a parameter such as the extent of ionization of the polyon will increase strongly the attractive forces if  $D_s > D$  and thus cause a tendency for  $\nu$  to increase. Since more segments now are deposited per polymer molecule, saturation is reached with fewer deposited polymer molecules, *i.e.*, at a lower capacity.

In studying polyelectrolyte adsorption, particularly at higher concentrations and varying ionic strengths, it must be remembered that polyelectrolyte not only competes for surface sites with the solvent but also with all the other ionic species in solution including any introduced by the substrate itself. Thus the surface charge density  $\sigma$  itself may vary drastically in the course of the adsorption and at arbitrary  $\theta$   $\sigma$  now must be taken as due to both adsorbed micro- and macro-ions. We already have mentioned effects due to relatively sudden changes in shape of the polymer molecule with the extent of ionization. This certainly can drastically affect  $\nu$ , particularly for the more rigid polymers.

Since a large number of segments has to be deposited per polymer molecule an adsorption isotherm like that suggested for non-polar macromolecules<sup>6</sup> is indicated. In any case the Langmuir isotherm is a special case of this class of isotherms.

**4. Relation to Experiment.**—It has been the major purpose of this paper to point out the nature of the various types of electrostatic interactions which affect the polyelectrolyte adsorption affinity  $K$ , as well as to estimate their relative contribution to this quantity for the rod-like macromolecule model. In view of our results, the ideal experiments with which quantitatively to compare our theory would determine  $K$  as a function of  $pH$ , at constant ionic strength or  $\kappa$ . Separate determinations, also at constant  $\kappa$ , are of course required for the  $pH$  dependence of the  $\alpha$ 's and of  $\sigma$ .

We readily acknowledge that the most serious limitation of the present model computation lies in the rigid rod assumption concerning coil conformation. Many polyelectrolytes (those with a helical structure, well known among proteins) come rather close geometrically to this ideal. Others, however, have a random coil structure whose appearance is quite different. In any event, the major effect of coil geometry lies in the value of the affinity for the uncharged polymer, as exhibited in eq. 2.3, because this quantity contains the entropy lost in properly orienting the coil (whatever its form) at the surface for adsorption to take place. Each of the additional electrostatic contributions to the actual affinity, on the other

hand, show only modest sensitivity to coil geometry; in fact, of the four contributions (2.7), (2.8), (2.11), and (2.13) to the work of bringing  $N\alpha$  charged groups up to the interface, only the third has explicitly utilized the rod assumption. A less regular coil would still possess an analogous quantity to (2.11) where the summation

$$\sum_{j=1}^{\infty} \frac{e^{-\kappa ja}}{\kappa ja}$$

has been replaced by a more general expression taking into account the less regular distribution of charge-charge distances adsorbed on the surface. The qualitative effects of  $\kappa$  and dielectric constant variation of the more general version of (2.11), however, remain unchanged upon relaxing the rod assumption. The two reasons for presenting these computations for the rigid rod model therefore are: (1) The impossibility of exhibiting for all contributions explicit results for  $\kappa$  and dielectric constant effects on the affinity except for this simple case. (2) The insensitivity of these electrostatic contributions to the actual coil geometry.

Suitable detailed experimental data appear to be rather scarce. That the electrostatic effects discussed in this paper often seem to be important, though, is evident from measurement of the stabilization of negatively charged gold sols by polycations, even at low added polyelectrolyte concentrations,<sup>2</sup> for the observations are indicative of the strong electrostatic tendency to adsorb on a surface not only charged oppositely to that of the ionized monomer units, but on a surface whose dielectric constant (infinity for gold, an electrical conductor) is greater than that of the solution. Accordingly, both expressions (2.5) and (2.13) are negative.

Miller and Grahame<sup>3</sup> furthermore apparently have observed the rapid onset of saturation of the adsorption isotherm of polyvinylpyridines on mercury surfaces, indicative of the power of attractive electrical image forces to constrain a polyelectrolyte to lie flat on the substrate, and therefore consume a large area available for adsorption.

Recently the affinity of aqueous polyacrylic acid onto anatase ( $TiO_2$ ) at the constant ionic strength of 0.1 has been measured as a function of  $pH$  between one and three  $pH$  units.<sup>4,14</sup> Fortunately, within this  $pH$  range estimates of  $\sigma$  from sedimentation rate studies indicate a less than twofold variation in  $\sigma$ , and  $\sigma$  is not tremendously large ( $\zeta \sim 20$  mv.).<sup>14</sup> Within the same  $pH$  range,  $\alpha$  (the extent of ionization) varies by a factor of 100.<sup>14</sup> The dielectric constant difference between the solution ( $D \sim 78$ ) and the substrate ( $D_s \sim 114$ ) is quite favorable ( $D_s > D$ ). Letting  $a = 3 \times 10^{-8}$  cm. and  $l \sim 0.5 \times 10^{-8}$  cm. we find that the four contributions to  $WD/N\alpha(Ze)^2$  are

$$\begin{aligned} \frac{1}{4l} \left( \frac{D - D_s}{D + D_s} \right) &\sim 10^7 \text{ cm.}^{-1} \\ F(\gamma)_\kappa &\sim 0.275 \times 10^7 \text{ cm.}^{-1} \\ -1.9 \times 10^4 \text{ cm.}^{-1} &\leq -\alpha \left( \frac{D - D_s}{D + D_s} \right) \frac{1}{a} \ln(1 - e^{-\kappa a}) \end{aligned}$$

(12) H. L. Frisch, *J. Phys. Chem.*, **59**, 633 (1955).

(13) W. I. Higuchi, *ibid.*, **65**, 487 (1961).

(14) We are indebted to Professor F. R. Eirich and Dr. R. J. Lauria for supplying us with these data.

$$\leq -1.9 \times 10^2 \text{ cm.}^{-1} \text{ and}$$

$$\frac{4\pi\sigma}{\kappa Z e} \lesssim 10^7 \text{ cm.}^{-1}$$

Thus, the most important terms are due to the unshielded image work per ionized group and the work of bringing the charged rod up to the adsorbent surface. We expect, therefore,  $W$  to be a

linear function of  $\alpha$  with positive slope. Equations 2.14 and 2.15 suggest that in this case the affinity should increase rapidly with  $pH$ . Figure 1 shows a plot of  $\log [\log K + \text{constant}]$  vs.  $\log \alpha + \text{constant} \approx pH$  which is linear as expected in this case on taking the logarithm of (2.15). In the same  $pH$  range, at the constant ionic strength of 0.1, the capacity<sup>4,14</sup> decreases monotonically (cf. section 3).

## CHAIN TRANSFER CONSTANT OF VINYLPIRROLIDONE WITH DEXTRAN

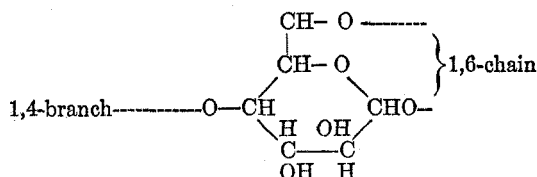
BY KWEI-PING S. KWEI<sup>1</sup> AND F. R. EIRICH

*Institute of Polymer Research, Polytechnic Institute of Brooklyn, Brooklyn, N. Y.*

*Received September 11, 1961*

The chain transfer constant of vinylpyrrolidone with a polymeric chain transfer agent, *e.g.*, dextran, was determined by modifying the conventional method to avoid the viscosity effect of the polymeric medium on the rate of polymerization. The chain transfer constant of vinylpyrrolidone with dextran was determined to be  $5.87 \times 10^{-4}$ .

In the course of our study of graft copolymerization of vinylpyrrolidone (VP) on dextran, initiated by azo-bis-isobutyronitrile in aqueous medium, the kinetics of the chain transfer reaction of the growing polyvinylpyrrolidone (PVP) chain radicals with dextran was examined. The latter, as a branched polyglucopyranose, contains tertiary hydrogen atoms and secondary hydroxy groups.



The chain transfer activity of low molecular weight secondary alcohols in the polymerization of styrene has been measured<sup>2</sup> and the secondary hydrogen on the carbon atom was found to be involved. Other chain transfer studies of alcohols<sup>3-5</sup> also confirm that displacement takes place on a hydrogen attached to the carbon bearing the -OH group. In addition, the C-H bonds in methylal have been found<sup>6</sup> to be activated by the two ether groups. Hence, the growing PVP chain radical likely will abstract a certain number of secondary or tertiary hydrogen atoms, leaving free radicals on dextran capable of initiating polymerization. We shall describe here a study of the rate of polymerization of VP and the chain transfer activity of VP chain radicals toward dextran.

### Experimental

The detailed procedure for the preparation of the PVP-dextran graft copolymer and the isolation and characterization of the respective homo- and copolymers has been de-

(1) Chemistry Department, Newark College of Engineering, Newark 2, New Jersey.

(2) M. Morton, J. A. Cala, and I. Piirma, *J. Am. Chem. Soc.*, **78**, 5394 (1956).

(3) C. T. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 285.

(4) R. A. Gregg and F. R. Mayo, *J. Am. Chem. Soc.*, **75**, 3530 (1953).

(5) W. R. Urry, F. W. Stacey, E. S. Huyser, and O. O. Juveland, *ibid.*, **76**, 450 (1954).

(6) K. P. S. Kwei and F. R. Eirich, *J. Polymer Sci.*, **53**, 81 (1961).

scribed previously.<sup>6</sup> A typical polymerization mixture consists of *n*-vinylpyrrolidone, dextran, azo-bis-isobutyronitrile, and water. All polymerization mixtures were rigorously degassed under high vacuum before use. The polymerization temperature was 50° and the total volume of each polymerization mixture was 50 ml. The polymerization time in each experiment was varied so that less than 5% conversion occurred. The molecular weight of PVP was determined from intrinsic viscosity measurements<sup>7</sup>

$$[\eta] = 5.65 \times 10^{-2} M_w^{0.55} \quad (1)$$

$$M_w = 197 [\eta]^{1.8} \quad (2)$$

at 25° in water.

### Results and Discussion

Even after repeated degassing of the polymerization mixture at  $10^{-6}$  mm. (4 times) a prolonged induction period was observed. Further degassing did not seem to reduce the length of the induction period. The presence of dextran in the polymerization mixture lengthens the induction period but does not appear to affect the rate of polymerization. Chain transfer of PVP chain radical with dextran, however, is evidenced by the decrease of the  $\overline{DP}$  of the free PVP homopolymer. Consequently, the conventional kinetic scheme was used.

$$1/\overline{DP} = 1/\overline{DP}_0 + C_s \frac{(S)}{(M)} + C_I \frac{(I)}{(M)} \quad (3)$$

Where

$$C_s = k_{tr,s}/k_p, \quad C_I = k_{tr,I}/k_p$$

$M$  = monomer,  $S$  = solvent,  $I$  = catalyst

$\overline{DP}_0 = \overline{DP}$  when no transfer agent is present

For azo-bis-isobutyronitrile, which does not chain transfer with PVP radicals, the third term of eq. 3 can be eliminated. Two "solvents" are present, namely, water and dextran, and chain transfer reactions to both may occur. The transfer to water probably can be neglected. The transfer constant,  $C_s$ , thus has been assigned to be that of dextran.

It is well known that the rate of polymerization changes if the viscosity of the medium is raised.<sup>8-10</sup>

(7) G. B. Levy and H. P. Frank, *ibid.*, **17**, 247 (1955).

(8) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 124.