[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE]

Interaction of Undissociated Polymethacrylic Acid and Polylysine with the Electrical Double-Layer on a Mercury Surface

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Differential capacities of the electrical double layer at the boundary between mercury and aqueous solutions of 0.09 *N* $NaClO_4$ + 0.01 *N* $HClO_4$ containing various concentrations of polymethacrylic acid (PMA) have been measured. Four different molecular weights of PMA have been used and the measurements carried out over a range of temperatures and frequencies. The results indicate the existence at the interface of a "surface phase" composed of molecules bound to the metal by a multiplicity of individually weak "bonds." The act of forming and breaking these "bonds" involves an activation energy presumed to be related to the associated reorientation of the adsorbed molecule. Two desorption peaks (*i.e.*, desorption as the potential moves away from that of the electrocapillary maximum) were obtained, one at a potential in a range between -1.1 v. for 0° and -1.15 v. for 80°, the other at a potential of about -0.05 v., both measured relative to a normal calomel electrode. The adsorption of PMA, unlike that of isobutyric acid, its monomeric analog, takes place even at very low concentrations, and the potential of the desorption peaks does not depend significantly upon the concentration. For polylysine, which is highly surface active, no desorption peaks could be observed over the range of potentials at which the measurements could be made. From the behavior of PMA, of polylysine and of isobutyric acid, the following conclusions concerning the character of polymeric adsorption on mercury were drawn. The adsorption energy of a polymeric molecule is built up additively from the adsorption energies of the adsorbed segments of the molecule. The rest of the segments of the adsorbed polymer are appended to the surface without touching it (*i.e.*, with negligible interaction), creating in the neighborhood of the surface a concentrated region which is called the surface phase. The packing of the segments of polymer in the adsorbed layer is never entirely close and undoubtedly depends upon the extent of coiling of the polymeric molecule.

Introduction

The adsorption of monomeric surface-active substances at the mercury–water interface has been extensively investigated in the past. Thus Gouy[2] measured the interfacial tension of mercury in contact with aqueous sodium sulfate solutions containing various organic substances and showed that the presence of such substances lowers the interfacial tension around the potential of the electrocapillary maximum (e.c.max.) and generally flattens the uppermost part of the electrocapillary curve. The potential of the e.c.max. was nearly always shifted, presumably as a result of the orientation at the surface of the dipoles of the adsorbed molecules. On both sides of the e.c.max. the electrocapillary curve changed slope more or less abruptly at certain potentials and thereafter was indistinguishable from the curve for the pure salt solution. The abrupt change in the slope of the electrocapillary curve corresponds to a peak in the differential capacity curve, as was pointed out by Gouy and first shown experimentally by Proskurnin and Frumkin.[3] This peak in the differential capacity curve results from the relatively abrupt desorption of the surface-active material as the potential is changed away from that of the e.c.max. In the neighborhood of the e.c.max., however, the differential capacity is low and shows a very shallow minimum. These phenomena have been extensively investigated in more recent times by Frumkin and his colleagues[4–6] and also to a lesser extent by Grahame.[7] Gorodetskaya, Frumkin and Melik-Gaikazyan have derived a relationship between the value of the differential capacity at its minimum and the thickness of the adsorbed layer.[5,8]

It has been the aim of the present work to investigate the behavior of polymeric surface-active substances at the mercury–solution interface. Differential capacity and electrocapillary measurements have been made for polymethacrylic acid (PMA) in acidic solution and for polylysine (PL) in alkaline solutions. The *p*H of the solution in the work here reported has been chosen to keep the polymers in the un-ionized condition. Thus electrostatic interaction of ionized polymers with the mercury surface was practically eliminated, and van der Waals forces, together with the associated orientation of molecular dipoles, were of major importance in the interaction of the polymeric molecules with the surface. We have tried to deduce from our experimental results the characteristics of the interaction of the polymers with the interface.

Experimental Part

The differential capacity of the mercury–solution interface was measured in an apparatus which has been developed and is described in detail elsewhere.[9] In brief, mercury droplets form at the tip of a thin-walled glass capillary (internal diameter *ca.* 0.02–0.04 mm., external diameter *ca.* 0.07 mm.) within the solution to be investigated, and an electrical double layer arises at the interface. The mercury droplet is surrounded by a platinum gauze sphere (2.5 cm. diam.) with holes at the poles to admit the capillary and to permit the escape of mercury. The platinum gauze sphere serves as a second electrode for the impedance measurements and also serves as an auxiliary potential-fixing electrode for the d.c. branch of the circuit. Its potential relative to the solution was monitored with a hydrogen electrode maintained in a separate compartment, and measurements were reckoned relative to the latter. The auxiliary Pt-sphere electrode served to keep the effective resistance of the d.c. branch of the circuit down to a few thousand ohms, which is helpful in many ways. The reference electrode was always held at 25°, while the temperature of the solution was maintained at any desired value from 0 to 80°.

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[1] On leave of absence from the Weizmann Institute, Rehovot, Israel, during the execution of this work.

[2] G. Gouy, *Ann. chim. phys.*, [8] **8**, 291 (1906); [8] **9**, 75 (1906).

[3] M. A. Proskurnin and A. N. Frumkin, *Trans. Faraday Soc.*, **31**, 110 (1935).

[4] V. I. Melik-Gaikazyan, *J. Phys. Chem.* (*U.S.S.R.*), **26**, 560 (1952).

[5] A. Gorodetskaya and A. N. Frumkin, *Compt. rend. acad. sci. U.R.S.S.*, **18**, 639 (1938).

[6] A. N. Frumkin and V. I. Melik-Gaikazyan, *Doklady Akad. Nauk S.S.S.R.*, **77**, 855 (1951).

[7] (a) D. C. Grahame, THIS JOURNAL, **68**, 301 (1946); (b) *Chem. Revs.* **41**, 441 (1947).

[8] V. I. Melik-Gaikazyan, *J. Phys. Chem.* (*U.S.S.R.*), **26**, 1184 (1952).

[9] D. C. Grahame, THIS JOURNAL, **71**, 2975 (1949); *CITCE*, **3**, 330 (1951); Technical Report No. 6 to the U. S. Office of Naval Research (May 25, 1951).

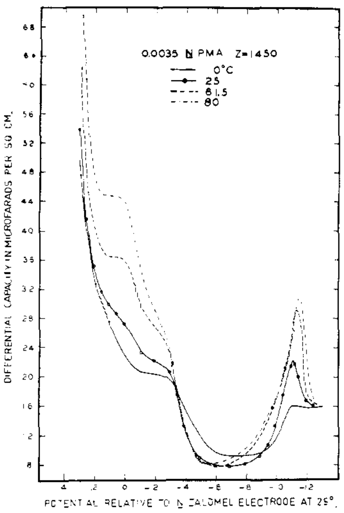

Fig. 1.—Differential capacity of Hg in contact with solutions of PMA as a function of temperature (and potential). Base solution is 0.09 *N* $NaClO_4$ + 0.01 *N* $HClO_4$.

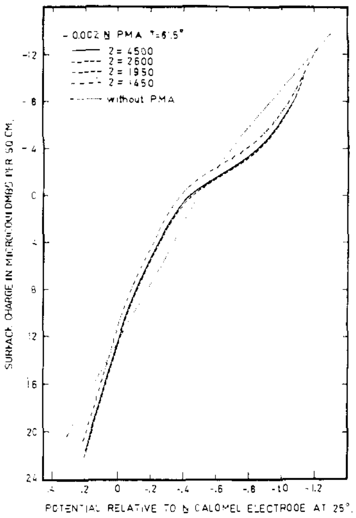

Fig. 6.—Surface charge density of Hg in contact with solutions of PMA and base solution.

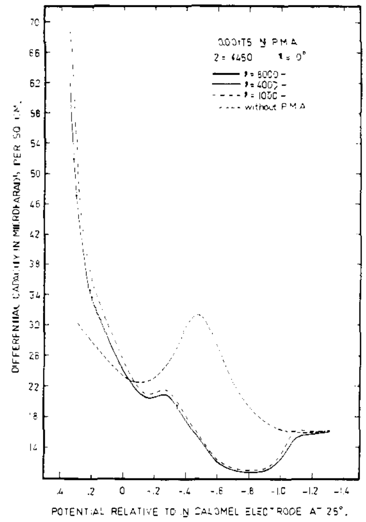

Fig. 12.—Differential capacity of 0.00175 *N* PMA at 0° as a function of the frequency of the measuring current.

The same apparatus was used for surface tension measurements, using either a drop weight method or a modification of the capillary rise method.[10] In the first method what was actually measured was the drop time, which is almost proportional to the drop weight in the region of interest. The timing was done electrically with an electric stopclock having a nominal accuracy of 0.002 sec. There was considerably more variability than this in the measured drop times, which we attribute to slight changes in the conditions at the tip of the capillary from moment to moment. In the second method we measured the least pressure needed to start the formation of a droplet at the tip of the capillary. As the capillary was slightly conical with its smallest diameter at the tip, at equilibrium the mercurostatic pressure at this point was equal and opposite to the upward pressure attributable to the surface tension. Any additional pressure causes the formation of a droplet. In the presence of polymers in the solution the first method was the more reproducible and gave results which appeared to be the more reliable, and therefore the results to be presented in Table I were obtained by its use.

In using the second method it was found that the potential at which droplets ceased forming depended upon the rate of change of the imposed potential. Besides that, in the critical region of potential a considerable time elapses between the fall of one droplet and the beginning of formation of the next, possibly in part because of a slow adsorption of capillary-active impurities from the solution but also and more probably because of the finite rate of diffusion of the polymer through the capillary to the interface. Whatever the reason, the second method was imprecise and possibly inaccurate as well. The same considerations apply in even greater degree to the conventional capillary electrometer, with the result that no steady readings could be obtained with it when polyelectrolytes were in the solution.

Solutions.—The base solution was always a tenth-normal aqueous salt–acid or salt–base solution. For solutions of polymethacrylic acid this was 0.09 *N* $NaClO_4$ + 0.01 *N* $HClO_4$ in conductivity water. This solution was then used also in the reference hydrogen electrode. Next to the fluoride ion, the perchlorate ion is probably the least adsorbed anion on positively charged mercury surfaces. This gives rise to a relatively low differential capacity on the anodic side of the e.c. max. and makes it possible to work over a wider range of potentials than would have been possible with solutions containing another anion.[11] Fluoride ion was not used in acid solutions for several reasons, of which the weakness of HF as an acid was the most fundamental.

In the study of polylysine solutions, the base solution used was 0.06 *N* NaF + 0.04 *N* NaOH in conductivity water. In this case the reference electrode contained 0.1 *N* NaF buffered to *p*H 7. In all cases the results will be reported relative to a normal calomel electrode (although such was not actually used) for the convenience of the reader.

The $NaClO_4$ and NaF used in these experiments were prepared by a twofold recrystallization from conductivity water of the C.P. materials. The PMA was kindly supplied to us by the Polymer Department and the polylysine by the Biophysical Department of the Weizmann Institute, Rehovot, Israel. Four different degrees of polymerization of PMA were employed. One of these samples having a nominal degree of polymerization, *z*, of 1450, gave results which can be more readily understood if it be supposed that the sample had in reality a much lower degree of polymerization. No mistake in the determination of the degree of polymerization could be uncovered, however, and it remains an open question whether the very considerable differences observed with samples of PMA having *z*-values of 1450 and 1950 are attributable solely to the difference in *z*. In all respects, the electrocapillary behavior of the sample of $z = 1450$ is consistent with that which would be expected for a polymer of considerably lower molecular weight. The other three samples had degrees of polymerization, *z*, of 1950, 2600 and 4500. The degree of polymerization of the polylysine was 60. In all of these polymers the half-width spread in the values of *z* was believed to be about ±7%.

Results with PMA

The four molecular weights of PMA were investigated first with respect to their effect upon the differential capacity of the double layer between mercury and aqueous solutions containing 0.09 *N* $NaClO_4$ + 0.01 *N* $HClO_4$, as stated above. Concentrations of PMA ranged from 0.0005 *N* (*i.e.*, 0.0005 monomole/liter) to 0.008 *N*. Some of the experiments were carried out at four different temperatures, 0, 25, 61.5 and 80°, but most measurements were made only at 0, 25 and 61.5°. At 80°, especially at the higher concentrations, the solutions became cloudy and the PMA started to precipitate. The experimental data for PMA with a degree of polymerization *z*, of 1450, at four temperatures and measured at a bridge frequency of 1000

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[10] D. C. Grahame, R. P. Larson and M. A. Poth, This Journal, **71**, 2978 (1949).

[11] D. C. Grahame, M. A. Poth and J. I. Cummings, *ibid.*, **74**, 4422 (1952).

cycles, are plotted in Fig. 1. For comparison the differential capacity of the pure salt solution for the same temperatures is shown in Fig. 2.

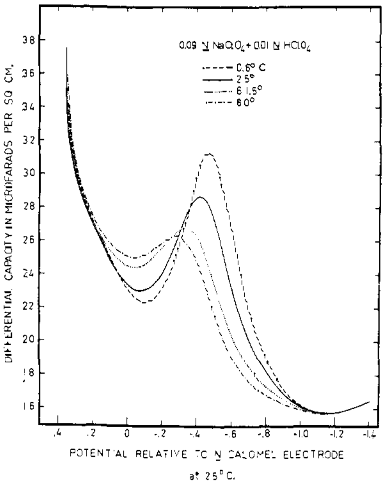

Fig. 2.—Differential capacity of base solution at various temperatures.

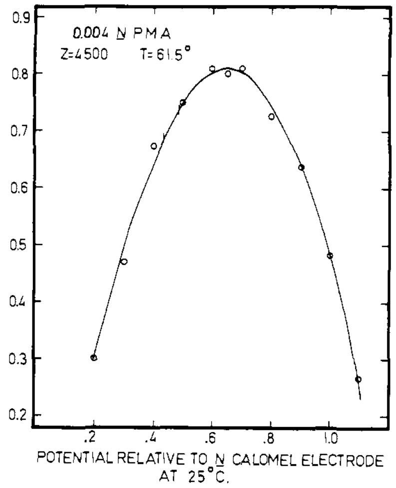

Fig. 14.—Degree of surface coverage, x, as a function of potential

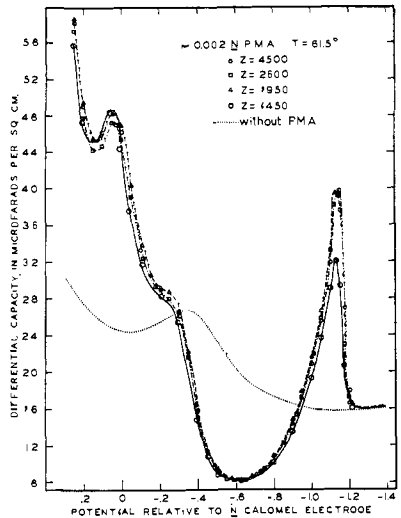

Fig. 3.—Differential capacity of PMA solutions at 61.5° as a function of degree of polymerization.

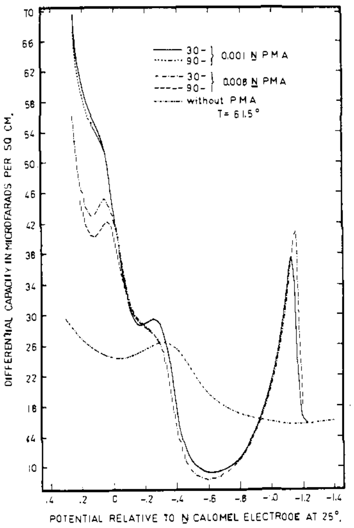

Fig. 8.—Differential capacity of PMA at 61.5° as a function of the frequency of the measuring current and as a function of concentration; z = 2600.

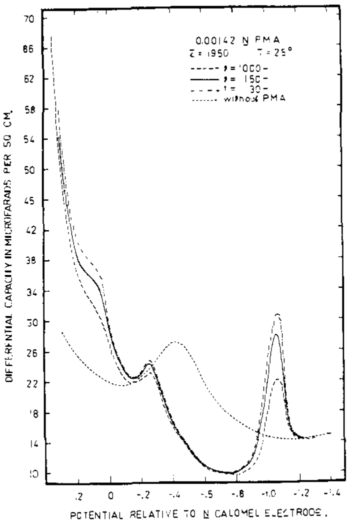

Fig. 13.—Differential capacity of 0.00142 N PMA at 25° as a function of the frequency of the measuring current.

It will be observed that the added PMA produces a region of low capacity, like other surface-active non-electrolytes, and that there is a strong desorption peak at about the same potential as is customarily observed with these substances. The height of this peak depends upon the temperature, a phenomenon which without much doubt indicates that below 80°, at least, the adsorption–desorption process which causes the peak is unable to keep pace with the 1000 cycle alternating potential used for the measurement. At 61.5° the results are *nearly* the same as at 80° in this region, however, which is taken to mean that at 61.5° the adsorption–desorption process which gives rise to the peak is nearly rapid enough to remain at equilibrium during the 1000 cycle excursions of the voltage. At lower frequencies, therefore, it will be deemed correct to proceed on the assumption of complete equilibrium with respect to the process which gives rise to the peak under these conditions.

It is of interest that the desorption peak nearly vanishes at 0°. This indicates that at this temperature the adsorption–desorption process is "frozen out" and practically unable to respond to the excursions of the alternating voltage. The curve at 0° therefore gives a measure of what has sometimes been called the "true" capacity, C_e, *i.e.*, the capacity of the covered and uncovered parts of the surface in parallel with no contribution from the adsorption–desorption process. This circumstance makes it possible to use the 0° curve to estimate the fractional coverage of the surface as discussed below.

It is occasion for some initial surprise that the minimum capacity observed in Fig. 1 is 18% larger at 0° than at the other temperatures investigated. Evidently the attainment of diffusion equilibrium at the surface is so much retarded at the lower temperature that the surface is less completely covered.

At still higher concentrations the minimum capacity at 0° approaches the minimum for the other temperatures. But even at the highest concentrations employed the shapes of the curves at different temperatures are expected (and found) to be different for the following reasons: (1) Lack of adsorption–desorption equilibrium at the lower temperatures (frequency effect); (2) the coils of PMA are more extended at low temperatures than at higher ones because the specific viscosity of PMA

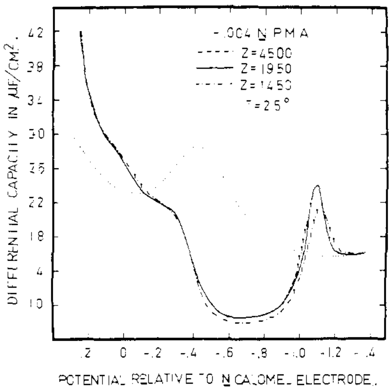

Fig. 4.—Differential capacity of PMA solutions at 25° as a function of degree of polymerization.

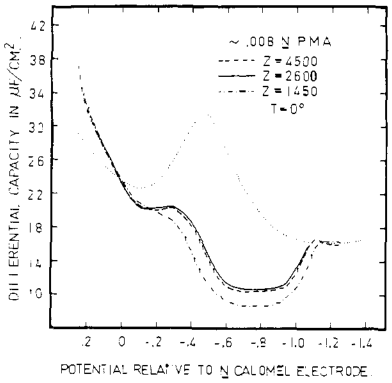

Fig. 5.—Differential capacity of PMA solutions at 0° as a function of degree of polymerization.

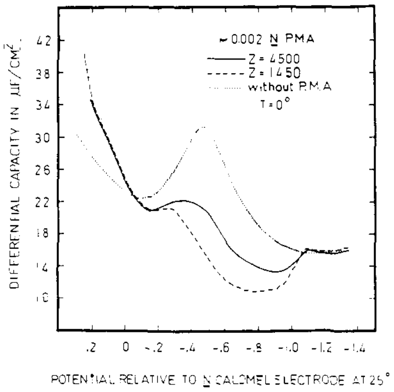

Fig. 11.—Differential capacity of ~0.002 N PMA at 0° as a function of degree of polymerization. Data obtained with insufficient time allowed for the attainment of diffusion equilibrium.

decreases with rising temperature[12]; (3) the capacity of the base solution depends upon the temperature (Fig. 2).

To the left of the minimum all the curves in Fig. 1 rise very steeply and soon surpass the values found for the base solution at the same temperature (Fig. 2). The "hump" in the capacity curves of the base solution is completely wiped out except possibly at 0°, where a plateau between 0 and -0.4 v. is presumably what remains of the very large hump observed in the absence of PMA. If a part of the surface remains uncovered, such an effect is to be expected. At temperatures above 0° the plateau is replaced by a point of inflection which becomes less pronounced as the temperature rises. The minor plateaus on the 61.5 and 80° curves are presumed to be desorption peaks, similar to those on the right but much less pronounced because of the phenomenon of "induced ionization" which makes the PMA behave as an anion in spite of the acid medium. Then the "induced anions" are adsorbed on the mercury like any other surface-active anion. This explanation also serves to account for the high values of capacity observed at the left-hand end of the curves and thus for the failure of the curves to approach the capacity curves for the pure base solution (Figs. 3-5).

The dependence of the capacity values on the degree of polymerization in the range of molecular weights at our disposal is rather small. As shown in Figs. 3-5, there is no clearly distinguishable difference in the behavior of the three polymers of highest molecular weights. The differential capacity curve in the presence of the smallest polymer, $z = 1450$, differs from the others in that at higher temperatures the height and area of the desorption peak (to be seen at a potential of -1.13 v. on the scale employed) are lower (Fig. 3). At 0° there is a similar difference in the depth of the "valley," which is the region where PMA is most strongly adsorbed (Fig. 5). This is to be expected from what has been said above on the view that the polymer of lowest z-value most readily comes to diffusion equilibrium with the mercury surface.

Assuming as usual for mercury surfaces that at very high negative potentials the surface-active material (*i.e.*, the PMA) is entirely expelled from the surface, the capacity, C, charge density, q, and interfacial tension, σ, for the solution containing PMA will be the same as for the pure base solution. This could be directly observed in the present experiments insofar as the capacity was concerned, and this fact made it possible to distinguish those potentials at which q and σ must also be identical with the pure solution values. Then if the measured capacity represents an equilibrium value of $\mathrm{d}q/\mathrm{d}E$ at all potentials, one should be able to obtain q as a function of E, the potential, by starting at some sufficiently large negative potential and integrating backwards toward the potential of the e.c.max. Then $\Delta q = \int C\,\mathrm{d}E$ and the potential of the e.c.max. is found as the value for which $q = 0$. In Table I the e.c.max. potentials obtained in this way are compared with the values obtained by surface tension measurements.

The assumption that the q in $\mathrm{d}q/\mathrm{d}E$ is the equilibrium value cannot be made without due consideration, however, because it implies that the system remains at equilibrium as regards adsorption and desorption of segments of the polymer molecules during the rapid changes of voltage represented by the imposed small alternating potential used for the measurement. This assumption can be tested in part by finding out whether or not the capacity is independent of the frequency, since a *small* time lag in the attainment of equilibrium will produce a dispersion (change with frequency) of the capacity. Dispersion was absent from our measurements at elevated temperatures (61-80°) and low frequencies and also at high frequencies and low temperatures. In this latter case the equilibrium is "frozen," and the differential capacity has a very different significance, as explained above. In the former case only it should be possible to ascertain the potential of the e.c.max. by back integration.

The values of the e.c.max. obtained in this manner are not in agreement with those obtained by the drop-time method, however, as Table I shows. The discrepancy is always in the same direction and

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(12) A. Silberberg and J. Eliassaf, private communication.

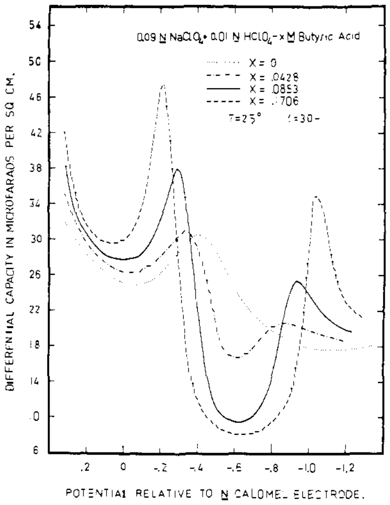

Fig. 7.—Differential capacity of x M butyric acid in contact with base solution.

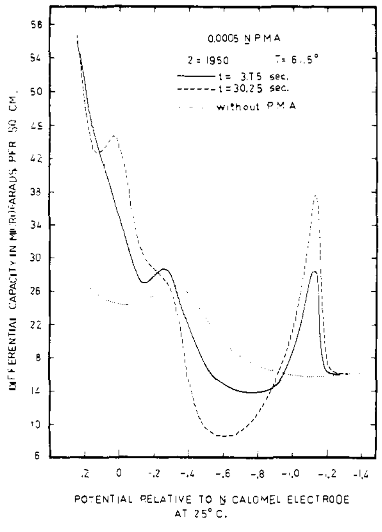

Fig. 9.—Differential capacity of 0.0005 N PMA after different amounts of time allowed for the attainment of diffusion equilibrium.

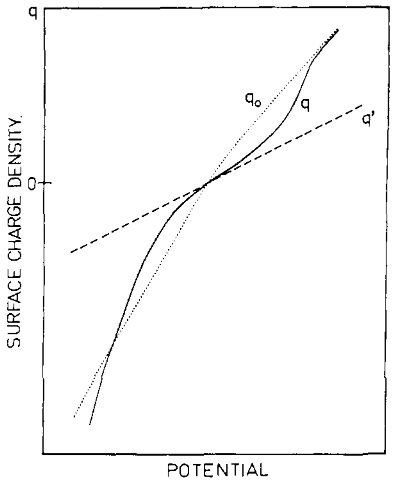

Fig. 15.—Schematic representation of the manner in which q, q_0 and q' vary with potential.

amounts to 51 mv. on the average. Experience with both of these methods leads us to trust the values obtained by the integration of the capacity and to distrust the values obtained by the drop-weight method when these disagree, and for that reason only the results of the former method will be used in subsequent calculations. The discrepancy does not affect any of the conclusions to be drawn, although it does alter the values of q, the surface charge density, by small fixed amounts. The surface charge density values for solutions containing approximately 0.002 monomole per liter are plotted as a function of potential in Fig. 6. (The dependence of the differential capacity as well as of the charge density on the concentration of the solution is minute, and the small differences in the concentrations of the different polymers (Table I) are insignificant.) Essentially the same charge density *vs.* potential curves were obtained for other concentrations of PMA and are therefore not presented. As Fig. 6 shows, the three samples of highest molecular weight all give practically the same curve of q *vs.* E.

Monomeric and Polymeric Behavior.—The monomer corresponding to PMA is isobutyric acid. As may be seen from Fig. 7, isobutyric acid changes the differential capacity of the mercury–solution interface only when present at quite high concentrations. This was to be expected, of course, for a substance of this low molecular weight. The shape of the curve and the position of the desorption peaks change very much as the concentration is raised fourfold, in marked contrast to the behavior of PMA. The distance between the peaks increases from 550 mv. at 0.0426 M to 825 mv. at 0.1706 M. This increase with concentration in the spread between the desorption peaks is general for monomeric surface-active materials and is usually explained by considering that the solvent molecules (with a relatively high dipole moment) compete for position at the interface with the surface-active molecules (of lower dipole moment). At higher concentrations of surface-active molecules the solvent molecules naturally require a higher field strength to displace them, in agreement with the observed result.

TABLE I

E.C.MAX. OF 0.09 N $NaClO_4$ + 0.01 N $HClO_4$ IN THE PRESENCE OF VARIOUS CONCENTRATIONS OF PMA AT 61.5°

		E.c.max. (rel. to normal calomel electrode)[a], v.	
z	Concn., N	By integration of C dE	By drop-time measurement (surface tension)
1450	0.00088	−0.370	−0.420
1450	.00175	− .369	− .425
1450	.0035	− .342	− .410
1450	.0070	− .348	− .395
1950	.0010	− .431	− .448
1950	.0020	− .435	− .468
1950	.0040	− .421	− .463
2600	.00098	− .427	− .500
2600	.00197	− .422	.....
2600	.00789	− .436	− .480
4500	.00197	− .427	− .490
4500	.00394	− .412	− .493
4500	.00789	− .418	− .480
Butyric acid at 25°	.0213	− .503	− .513
Butyric acid at 25°	.0426	− .468	− .491
Butyric acid at 25°	.0853	− .382	− .448
Butyric acid at 25°	.1706	− .335	− .417

[a] E.c.max. values of the pure "salt" solution (*i.e.*, without PMA) at 61.5° obtained from surface tension measurements were −0.495, −0.500, −0.496 and −0.494. Average: −0.496 v. relative to N calomel electrode. E.c.max. of the same solution obtained by the integration of C dE was −0.495 v.

Although the potential of the e.c.max. remains in doubt, the values obtained by the integration of the capacity are probably nearly correct. But whichever set of values is correct, it is clear from the results that the addition of PMA shifts the potential by a surprisingly small amount. Excluding the results for the polymer for which z = 1450, the shift is never more than 83 mv. and averages 70 mv. This is to be contrasted with the considerably larger shift given by solutions of isobutyric acid in concentrations sufficient to build up the better part of a monolayer. Thus a 0.1706 *N* solution of isobutyric acid shifts the potential of the e.c.max. by 160 mv., whereas a 0.004 *N* solution of PMA (adsorbed to about the same degree) shifts it by 83 mv. or less. (It will be shown subsequently (Fig. 14) that about 70% of the surface is covered with adsorbed segments of PMA under these conditions.)

The shift in the potential of the e.c.max. results from the adsorption of segments of PMA or of molecules of isobutyric acid and the desorption of water molecules whose places are occupied. In addition it must be remembered that the adsorbed molecules will have a different, and generally larger, polarizability than the displaced water. This tends to counteract the "natural" field of the metal[13] and shifts the potential of the e.c.max. in the direction found. When a monomeric substance is adsorbed, each molecule can line up in the "natural" field of the metal, but the segments of a polymeric substance are constrained by their interlinkage to reach some sort of a compromise. It is clear that this compromise decreases the shift in the e.c.max. when compared with the behavior of the unrestricted monomer of comparable structure.

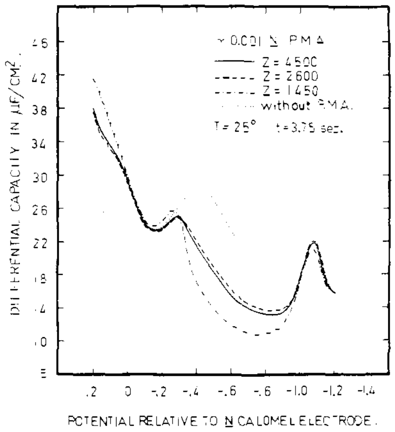

Fig. 10.—Differential capacity of ~0.001 *N* PMA at 25° as a function of degree of polymerization. Data obtained with insufficient time allowed for the attainment of diffusion equilibrium.

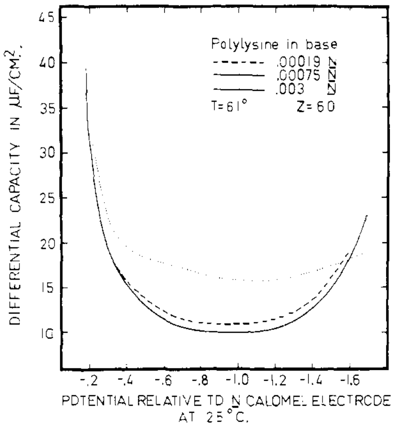

Fig. 16.—Differential capacity of polylysine as a function of concentration and potential.

Figure 8 shows that the potential of the cathodic peak for PMA (unlike the monomer) does not shift significantly with concentration over the range of concentrations there represented. At still lower concentrations (0.0005 *N*) the capacity becomes markedly dependent upon the age of the mercury drop (Fig. 9), however. This is clearly a case of too-slow adsorption, undoubtedly because of diffusion control. In this connection it is noteworthy that the capacity was not frequency dependent even when diffusion equilibrium had not been achieved. In the case shown it took more than 4 seconds to develop the full size of the desorption peak; also the shape of the rest of the curve indicates that adsorption was not completed even during a four-second exposure of the mercury droplet to this very dilute solution. This is therefore a case of diffusion control.

There is a seeming paradox here which requires explanation. The lack of any dispersion of the capacity in the peaks shows that the adsorption–desorption process which gives rise to them is not diffusion controlled in spite of the fact that the diffusion of the polymeric molecules to the surface is a relatively slow process, requiring times of the order of seconds to reach equilibrium from solutions of the concentrations here employed. This result is explained by assuming that there exists at the interface a region of high polymer concentration, to be called the surface phase, and that the peaks result from the adsorption and desorption of *segments* of the polymer from the surface phase. This process need not wait upon the diffusion of whole polymer molecules from the solution and is at elevated temperatures fast enough to keep pace with a signal of low audio frequency. The individual segments are presumably rather loosely bound, although many segments of a given molecule may be bound simultaneously, giving a large net adsorption energy.

The postulate of the existence of a surface phase is not actually a new postulate at all, since it is merely the polymeric analog of the monolayer of monomeric substances which is known to form under similar conditions.

The lower the temperature, the higher the concentration needed to obtain diffusion equilibrium in a given time. As shown in Fig. 10 for 25° and in Fig. 11 for 0° the polymer of lowest molecular weight comes to equilibrium more readily than do the others. These observations again point to diffusion as the rate-limiting process.

The diffusion coefficient of unionized PMA is expected to decrease with the square root of the degree of polymerization. The virtual identity in the rate of achieving equilibrium in the case of the three samples of higher molecular weight probably means only that the sensitivity of this rather rough method of observing the approach to equilibrium is not such as to reveal a difference in diffusion rates of a factor of only 1.5.

It can be shown by a simple extension of equation 17 in reference 7b that

$$d\sigma = -q\,dE^- - \frac{\Gamma_+}{\nu_+}\,d\mu - \Gamma_{ne}d\mu_{ne} \qquad (1)$$

where Γ_{ne} is the "superficial density" (the term used by Gibbs) of non-electrolyte and μ_{ne} is its chemical potential. The other terms in equation 1 are defined in reference 7b. Briefly, Γ_+ is the superficial density of cations (referred to a plane for which $\Gamma_{solvent} = 0$), ν_+ is the number of cations formed

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(13) D. C. Grahame, *Z. Elektrochem.*, **59**, 740 (1955).

by the dissociation of one molecule of the electrolyte present, μ is the chemical potential of this electrolyte, σ is the interfacial tension and q is the surface charge density. E^- is the potential of a polarized electrode measured relative to an electrode reversible to the anion of the electrolyte. In the experiments here under consideration μ is substantially constant and E^- likewise when points at the same measured potential are compared. Thus under these circumstances

$$\mathrm{d}\sigma/\mathrm{d}\mu_{\mathrm{ne}} = -\Gamma_{\mathrm{ne}} \tag{2}$$

and after differentiation twice with respect to E

$$\mathrm{d}^3\sigma/\mathrm{d}E^2\mathrm{d}\mu_{\mathrm{ne}} = -\mathrm{d}^2\Gamma_{\mathrm{ne}}/\mathrm{d}E^2 \tag{3}$$

But by the Lippmann equation $\mathrm{d}\sigma/\mathrm{d}E = -q$ at constant composition, and therefore $\mathrm{d}^2\sigma/\mathrm{d}E^2 = -\mathrm{d}q/\mathrm{d}E = -C$, where C is the differential capacity. Accordingly

$$\mathrm{d}C/\mathrm{d}\mu_{\mathrm{ne}} = \mathrm{d}^2\Gamma_{\mathrm{ne}}/\mathrm{d}E^2 \tag{4}$$

The quantity on the left is nearly zero over a long range of potentials, as can be seen from Fig. 8, which is representative of many such measurements. This means that $\mathrm{d}\Gamma_{\mathrm{ne}}/\mathrm{d}E$ is nearly constant in the region where the capacity is nearly independent of the concentration. It seems clear that the constant in question is zero, since otherwise there would have to be a linear change of Γ_{ne} with E which there is no reason to expect and for which there is no evidence. On the other hand, a zero value of $\mathrm{d}\Gamma_{\mathrm{ne}}/\mathrm{d}E$ leads to a constant value of Γ_{ne}, which is just what one has to expect over the range of potentials in question in view of the fact that a molecule held by one point of attachment is just as much at the interface as one held by many. The experimental data are then consistent with a picture for which Γ_{ne} is zero to the right of the desorption peak, goes rather suddenly to a constant value representative of the surface phase, and finally goes to lower values at positive potentials where desorption sets in. (The large negative values of $\mathrm{d}C/\mathrm{d}\mu_{\mathrm{ne}}$ found in this region and shown in Fig. 8 were observed consistently and indicate the onset of desorption.)

The above interpretation of the capacity data calls for rather large values of $\mathrm{d}C/\mathrm{d}\mu_{\mathrm{ne}}$ at the potential of the cathodic desorption peak. This shows that it is theoretically necessary to have some shift in the potential[14] of the peak with change in concentration of the polyelectrolyte, but because the capacity curves are steep, this shift does not have to be very large. The experimental data are not sufficiently precise to permit a meaningful calculation of Γ_{ne} from the observed changes in the potential and height of the desorption peaks.

The adsorbed polymeric molecule is certainly not spread flat in the surface since thorough flattening of the molecule would enormously decrease the configurational entropy of the molecule. Hence only a part of the segments are adsorbed; the rest of the molecule remains only indirectly attached to the surface and forms together with the neighboring molecules the concentrated layer which we have called the surface phase.

Frequency Dependence at Different Temperatures.—If the adsorption and desorption processes are somewhat slow with respect to the period of variation of the potentials of the alternating current used for the bridge measurements, the measured capacities are a function of the frequency of the alternating current. This frequency effect can give some idea about the mechanism of the adsorption process. Frumkin and Melik-Gaikazyan[4,6] were able to show that for monomeric surface-active substances diffusion to the surface is the slowest step and therefore the determining factor in the adsorption mechanism at the surface. Consequently in this case the dispersion of the capacity decreases with increasing bulk concentration of the surface-active material. On the other hand, the bulk concentration of a polymeric substance has no influence on the frequency effect at the cathodic desorption potential. For example, at 61.5° and low frequencies there is no observed frequency dependence even though there is a dependence of the measured capacity on the age of the mercury surface (Figs. 8 and 9). At 25°, where the frequency effect is pronounced, it nevertheless remains constant for large variations of concentration and molecular weight (Fig. 13). Complete lack of dependence of the frequency effect on the bulk concentration indicates that no significant diffusion of whole polymeric molecules takes place during the variation in potential of the imposed alternating voltage. Hence the frequency effect must depend upon the rate of migration of adsorbable segments *from the surface phase* into the adsorption layer and *vice versa*, as stated above. Migration of segments can occur only in conjunction with rearrangement of the whole polymeric molecule; consequently, the temperature dependence of the dispersion is expected to be far stronger than in the case of unhindered diffusion of small molecules. Most probably the hindrance of hydrogen bonds to polymeric rearrangement also has much to do with this.[15]

While at 0° at high frequencies the desorption peak disappears completely (Fig. 12), at 61.5° at 90 and 30 cycles equilibrium values (between adsorbed and unadsorbed segments) are achieved and the peaks are fully developed (Figs. 8, 9). The frequency effect at 25° lies between that at 61.5 and 0° (not shown).

It is of interest to compute the fraction x of the surface covered by the adsorbed segments of the polymer under any given set of conditions. This can be done in either of two ways, each of which involves certain reasonably plausible assumptions. In the cases tried, the two methods agreed to within about 5 or 10%.

The first method employs the equation

$$C_{\mathrm{e}} = xC'_{\mathrm{e}} + (1 - x)C^{\circ}$$

where C_{e} is what Melik-Gaikazyan, who has also used this method,[4] calls the "true" capacity of the double layer. This is the capacity which would be observed if the adsorption–desorption process could be completely inhibited. C'_{e} is the "true" capacity of a completely covered surface and C° that of the bare surface. The first has been esti-

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(14) The potential, and not merely the height, has to change because $\mathrm{d}C/\mathrm{d}\mu_{\mathrm{ne}}$ has to have both positive and negative values so that $\mathrm{d}\Gamma_{\mathrm{ne}}/\mathrm{d}E$ can be zero on both sides of the desorption peak.

(15) I. R. Miller, *J. Coll. Sci.*, **9**, 579 (1954).

mated here by using data of Melik-Gaikazyan[4] for the capacity of the double layer saturated with a monolayer of butyl alcohol, this alcohol having the same number of carbon atoms as the side chain of PMA, and the second is the capacity observed in the absence of the polymer. The equation assumes that the unadsorbed segments of the polymer have negligible effect upon the capacity of the "bare spots" on the surface. In the above equation, all of the C-values must naturally correspond to the same over-all potential. It is assumed that C_e' is unaffected by the potential, which seems to be substantially true in the case of octyl alcohol, for instance.[7] In practice C_e can be found either by lowering the temperature or by raising the frequency of the alternating potential to so large a value that the adsorption–desorption process cannot follow it. We were not able to make accurate measurements at sufficiently high frequencies to obtain C_e in this manner at 61.5°, but by inspection of the low-temperature capacity curves, it was rather easily possible to estimate the high-frequency limit at higher temperatures and thus to obtain C_e at these temperatures. In this manner the values of x shown in Fig. 14 were obtained.

The second method employs the equation[16]

$$q = xq' + (1 - x)\,q_0$$

where q is the surface charge density of the partially covered surface, q' is the surface charge density of a fully covered surface and q_0 is that of a bare surface. All of the q's refer to the same over-all potential.

When $q' = q_0$, q is independent of x and equals both. Hence there should be a common point of crossing of curves representing q as a function of potential. This is shown schematically in Fig. 15. Through the point of crossing of q and q_0, one can draw a line of slope C_e', and this is q'. Then one has everything needed for the calculation of x. The two methods are not wholly independent in that both require a knowledge of C_e'. The results of the calculation are in agreement with those shown in Fig. 14. The surface is never completely covered, and the degree of coverage falls off rapidly on either side of the maximum, which lies on the cathodic side of the e.c.max. (whose potential as determined by the two methods discussed earlier is shown by two vertical lines on the figure).

It is of interest that the variation with potential in the values of x found in this manner do not agree with our above-made estimate of the variation with potential in the values of Γ_{ne}. Thus x and Γ_{ne} are not proportional and cannot be regarded as two measures of the same thing. This disagreement is not a consequence of minor experimental errors but is implicit in the shape of the capacity curves themselves, which should be flat over a considerable range of potentials if x were constant and close to unity. This is, in fact, the usual behavior of solutions of surface-active monomers.[3-7] The difference here arises from the fact that an adsorbed polymer molecule may be bound to the surface by one or by many points of adsorption. Γ_{ne} is the same for a monolayer in either case, but if the exclusion of the ions of the base electrolyte and of the solvent only occurs at the points of adsorption, than the "degree of coverage," x, will vary even while Γ_{ne} remains constant. This seems to be the case and accounts very well for the observed behavior. Probably the segments of the polyelectrolyte behave very much like monomers as regards their ability to exclude the ions of the electrolyte and the solvent, but because they are interconnected, Γ_{ne} is kept reasonably constant over a considerable range of potentials.

Results with Polylysine

Polylysine is a fairly strong base, and in order to keep it in the un-ionized state a solution containing 0.04 N NaOH and 0.06 N NaF was used. As lysine itself has a relatively long hydrocarbon chain (5 carbons), the polymer must have a rather high specific adsorption energy, and thus it happens that no desorption peaks could be observed. The capacity values decreased with increasing polylysine concentration until a limiting value was reached at about 0.00075 N (Fig. 16).

In spite of the fact that the side chain in polylysine is considerably larger than in PMA,[17] the limiting minimum capacity value in the presence of the former (about 10 μF./cm.^{2} at 61.5°) is significantly higher than in the presence of the latter (8 μF./cm.^{2} at 61.5°). This result could mean that the adsorbed side chains of polylysine have a higher effective dielectric constant than do those of PMA, or it could mean that the polylysine is less coiled than PMA. The long side chains of polylysine hinder the coiling and therefore increase the length of the statistical element. This property of polylysine makes a looser packing in the surface very plausible, which would permit more water and thereby more ions to approach the surface without hindrance, thus giving rise to a higher capacity. This hypothesis could be checked by choosing for the base solution an electrolyte such as $NaClO_4$, which should give rise to a noticeable "hump," like that in Fig. 9, for instance. This technique could presumably be fruitfully used in the investigation of adsorbed organic layers in general.

Conclusion

Polymers in solution are strongly adsorbed on mercury and are in certain respects not very different in their behavior from monomers. Desorption peaks are observable where the hydrocarbon side chain is not too long, and the position of the peaks is essentially independent of concentration. Although diffusion of whole polymer molecules to and from the surface is expectedly slow, diffusion of segments of an already anchored molecule takes

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(16) NOTE ADDED IN PROOF.—This equation and the one just above become meaningless when x becomes negative. This happens at sufficiently anodic potentials, as Fig. 15 represents, and the reason for the failure of the equation is clearly that the phenomenon of "induced ionization" of the PMA has been ignored. For this reason, values of x computed with the aid of either of these two equations should be viewed with suspicion at anodic potentials (*i.e.*, to the left of the small vertical lines in Fig. 14).

(17) Concerning the polymerization of lysine, the ϵ-amino group is blocked by carbobenzoxy, and the polymerization takes place by decomposition of the anhydride, which involves only the α-amino group. Ref. E. Katchalsky in "Advances in Protein Chemistry," VI, Academic Press, Inc., New York, N. Y., 1951, p. 156.

place rapidly enough to permit the attainment of equilibrium in times of the order of hundredths of a second at 61°. This diffusion of segments is a process requiring activation energy, as is evidenced by its large dependence upon temperature. The electrocapillary properties of polyelectrolytes can be investigated usefully by the differential capacity method and the degree of coverage of the surface can be determined. Evidence is cited which shows that the adsorbed segments of un-ionized PMA act individually in their ability to exclude the solvent and the ions of the electrolyte.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON]

Classification of π-Electron States[1]

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A classification of π-electron states is proposed in which two types are distinguished. The first type is described as involving resonance among normal structures. Empirical justification may be found in the spectra of dyes, radicals and aromatic hydrocarbons. The second is described as involving resonance among excited structures. States of this type are reached in transitions in the carotenoid pigments. The spectra of benzene, azulene and naphthalene are examined and the various states classified as belonging to one or the other of the two types under consideration.

Introduction

In this paper it will be shown that 2p(π) valence shell states may profitably be classified into two types: states of the first type arise from resonance among valence bond structures, and include the ground state; states representing the second type arise from a migration of excitation energy considered localized initially in a double bond. This will be said to result from resonance among excited structures.

The importance of classification theory has been discussed by Platt[2]; and the classification of π-electron states and transitions has already been carried out in several different ways. These include classification into long and round field spectra,[3] differentiation of the α and *p* bands of Clar[4] (*e.g.*, involving transition to the B_{2u} and B_{1u} states of benzene) and recent emphasis on the importance of differing amounts of configuration interaction.[5] (The first and second π-electron excited states may often be classified as different from each other owing to the fact that the first excited state is chiefly a single configuration, while the second is in essence not a single configuration.)

The method of classification to be described here is on the surface different from the others, though on closer examination it proves to be related. The present approach is phenomenological, and designed to conform as closely as possible to the classical theory of valence in chemistry.

The plan of the paper is first to make clear what is meant by the two different kinds of states, involving resonance among normal and excited structures. Next some of the simple aromatic hydrocarbons are considered, as examples of molecules having both types of states. In the course of the consideration of these examples some principles such as estimation of intensities and polarizations are brought in.

Resonance among Normal Structures.—"Normal structures" are structures in the context of the classical theory of valence which have the greatest stability. This would for example exclude the Dewar structures for benzene, and structures like the following

$$\overset{\ominus\cdot\cdot}{\mathrm{O}}\text{—}\overset{\oplus}{\mathrm{C}}\mathrm{H}\text{—}\overset{\cdot\cdot\ominus}{\mathrm{O}}$$

for formate ion. The energy of a structure is determined by the number and strength of bonds, stability of non-bonding electron pairs, etc., appraised in the usual intuitive fashion. This use of the classical theory of valence results in a certain amount of ambiguity as, for example, with amides, having the structures

$$\mathrm{R_2\ddot{N}}\text{—}\mathrm{CH{=}O},\quad \mathrm{R_2}\overset{\oplus}{\mathrm{N}}\mathrm{{=}CH}\text{—}\overset{\cdot\cdot\ominus}{\mathrm{O}}$$

Here the second structure might be classed as normal by analogy with the corresponding structure for formate ion

$$\mathrm{O{=}CH}\text{—}\overset{\cdot\cdot\ominus}{\mathrm{O}}$$

or, alternatively, as significantly less stable than the first. The difficulty with ambiguity has to be mentioned, but does not seem to be a serious problem in what follows.

Recent developments in molecular electronic state spectroscopy include the determination of the polarizations of bands for a number of key molecules. This now makes it possible to test the following *hypothesis:* Whenever, according to the classical theory of valence, there is more than one normal structure to represent a molecule there will be as many low-lying electronic states as there are structure, with symmetries appropriate to the wave functions from which the structures were derived. The formulation and testing of this *hypothesis* requires that a study be made of the prediction of symmetry species from structures or, equivalently, the polarizations of bands.[6]

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[1] This research was supported in part by the Air Research and Development Command under Contract AF 18(600)-375.

[2] J. R. Platt, *J. Opt. Soc. Am.*, **43**, 252 (1953).

[3] J. R. Platt, *J. Chem. Phys.*, **18**, 1168 (1950).

[4] W. Moffitt, *ibid.*, **22**, 320 (1954).

[5] The importance of this interaction has been recognized by a number of workers including Parr and Pariser, Moffitt and Dewar and Longuet-Higgins; R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).

[6] W. T. Simpson, THIS JOURNAL, **75**, 597 (1953); W. T. Simpson and C. W. Looney, *ibid.*, **76**, 6285 (1954).