conductances can be evaluated from properly related data for electrolytes containing either the $\mathrm{OctdMe_3N^+}$ or the $\mathrm{OctdSO_4^-}$ ion and for other electrolytes having common anions or cations. Table III contains values of limiting ionic conductances in NMA at 40° which are based upon this approximation method. Data from previous papers[3,4] were utilized also in order to provide an up-to-date comprehensive tabulation for NMA solutions.

The trimethylphenylammonium and the benzenesulfonate ions, like the $\mathrm{OctdMe_3N^+}$ and the $\mathrm{OctdSO_4^-}$ ions, are relatively large similarly-shaped species having comparable dimensions and are characterized by almost equal limiting conductances in aqueous solutions.[15,16] Consequently, it is worthwhile to note that the results in Table II would be altered less than 0.5% if $\mathrm{Me_3PhNO_3SPh}$ were used as the reference electrolyte instead of $\mathrm{OctdMe_3NOctdSO_4}$. On the basis of data for aqueous and NMA solutions, therefore, $\mathrm{Me_3PhNO_3SPh}$ is potentially applicable as a reference electrolyte for approximating limiting ionic equivalent conductances in other solvents. Inherent advantages may be utilized also inasmuch as $\mathrm{Me_3PhNO_3SPh}$, $\mathrm{NaO_3SPh}$ and $\mathrm{Me_3PhNI}$ are commercially available, easily purified and readily soluble in several common solvents in which $\mathrm{OctdMe_3NOctdSO_4}$ and $\mathrm{KOctdSO_4}$ are practically insoluble.

Based on the data in Table III, the limiting equivalent conductance–viscosity products for the $\mathrm{Bu_4N^+}$ and the $\mathrm{Pi^-}$ ions in NMA are 0.236 and 0.356 ohm^{-1} cm.^{2} equiv.$^{-1}$ poise and are about 35% greater than the corresponding products for aqueous solutions. Nevertheless, the ratio of the limiting equivalent conductance of the picrate ion to that of $\mathrm{Bu_4N^+}$ ion in NMA differs less than 3% from the same conductance ratio for aqueous solutions and consequently indicates considerable parallelism in the relative conductance behavior of these large ions in NMA and in water.

Although the ratio of the viscosity of NMA at 40° to that of water at 25° is 3.4, the ratio of the limiting equivalent conductance of an ion in water at 25° to that of the same ion in NMA at 40° varies from 2.5 for the $\mathrm{Bu_4N^+}$ ion to 8.7 for the potassium ion, excluding the solvated proton and several ions for which proper comparison data are unavailable. The broad range of values for the conductance ratio together with the very high values for the conductance–viscosity products for the $\mathrm{Bu_4N^+}$ and $\mathrm{Pi^-}$ ions suggests that unusual relative solute–solvent interactions and perhaps significant variations between the macroscopic viscosities of the solutions and the microscopic viscosities in the immediate vicinities of the ionic species may be operative in NMA solutions. Novel positions which are occupied by several ionic species in series of decreasing cationic and anionic limiting equivalent conductances are readily discernible from the data presented in Table III.

In comparing the behavior of hydrogen chloride and 2,4,6-trinitrophenol (picric acid) in the isomeric amides, N-methylacetamide and N,N-dimethylformamide, it is interesting to note that the former and the latter[8] act as leveling and differentiating solvents, respectively, toward the acidic solutes. The extent of substitution on the amide-N not only drastically affects the magnitudes of physical properties but also apparently is reflected in the proton-accepting properties of the medium.

Other conductance studies involving the behavior of multivalent electrolytes in NMA and also the behavior of uni-univalent electrolytes in iso-viscous mixtures of NMA and tertiary butyl alcohol and in mixtures of isomeric NMA and N,N-dimethylformamide are in progress in this Laboratory.

LEXINGTON, KENTUCKY

[15] W. J. McDowell and C. A. Kraus, THIS JOURNAL, **73**, 2173 (1951).

[16] G. H. Jeffery and A. I. Vogel, *J. Chem. Soc.*, 400 (1932).

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

Interaction of Polyelectrolytes with the Electrical Double Layer on Mercury–Water Interfaces. II. Influence of Added Ionized Polyacids on the Differential Capacity*

BY ISRAEL R. MILLER[1] AND DAVID C. GRAHAME

RECEIVED NOVEMBER 23, 1956

The differential capacity of the electrical double layer at the interface between mercury and aqueous 0.1 *N* NaF solutions containing various amounts of the salts of dibasic and polybasic acids at different temperatures has been measured. A series of polyacids has been investigated, starting with simple dibasic acids, through the relatively low molecular weight polyaspartic and polyglutamic acids, and extending finally to very high molecular weight samples of polymethacrylic acid of various degrees of polymerization. It has been found that the results can be interpreted by assuming (a) that even short hydrocarbon chains produce a squeezing-out effect which appears as an adsorption of anions, and (b) that polybasic anions are completely expelled from the interface when the mercury carries even a small negative charge, and strongly attracted when the charge is slightly positive. Adsorption–desorption peaks are produced at the potential of the electrocapillary maximum through the operation of this effect. It seems clear that a monolayer of anions is formed.

Introduction

From the electrocapillary properties of soluble acetates and oxalates it is known,[2-4] that the car-

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* Reproduction in whole or in part permitted for purposes of the U. S. Government.

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

[2] G. Gouy, *Ann. chim. phys.*, [7] **29**, 145 (1903).

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

[4] D. C. Grahame and B. A. Soderberg, *J. Chem. Phys.*, **22**, 449 (1954).

boxylate ion is little or not at all adsorbed on an uncharged mercury surface. The object of the present work has been to investigate the coöperative influence of a series of carboxylate groups located on a polymeric chain. The plan has been to start with the simplest dicarboxylate ion, oxalate, and to work up to ionized polymethacrylic acid in easy stages.

The adsorption of ions on mercury takes place in four somewhat different ways, and it is helpful to have these in mind even though it is not always possible to sort them out experimentally. There is, in the first place, simple electrostatic attraction (Type I adsorption). On an uncharged surface this type of attraction is deemed absent, and whatever adsorption is found is attributed to something else.

Electrostatic attraction gives rise to the diffuse double layer, whose mathematical exposition was given by Gouy and Chapman, but the effects of electrostatic attraction are not wholly predictable by means of that theory because the ions in question have a finite distance of closest approach to the interface, and the thickness and dielectric properties of this "inner region" of the double layer are of controlling importance in most cases, as was first pointed out by Stern. These properties are not even yet fully understood, although they have formed the subject of many publications.[5]

A second type of adsorption of ions (to be called Type II) is related to what is commonly called chemisorption. Many anions form chemical bonds with mercury, the strength of the bond depending upon the surface charge density. The concept of adsorption on mercury as chemical bond formation was clearly stated as long ago as 1908 by Gouy.[6] The ions which show this phenomenon most strongly ($S^=$, I^-, SCN^-, Br^-) are those which form highly insoluble salts with mercury, and the two phenomena are obviously related. One can say either that a covalent bond is formed between mercury and the anion, or one can attribute the attraction to the polarizability of the anion. Undoubtedly a large polarizability leads to strong covalent bond formation, so that the two statements are equivalent.

Type II adsorption is most clearly recognizable at the potential of the electrocapillary maximum (e.c.max.) because Type I adsorption is then absent. The adsorption of anions (from whatever cause) lowers the surface tension and shifts the potential of the e.c.max. toward more cathodic values. A more distinctive test for Type II adsorption lies in the rather rapid rise in the differential capacity which occurs as the surface is positively charged, but since this also happens with Type I adsorption of bivalent and polyvalent ions (especially when the charge is concentrated at the center of an ion, as in $SO_4^=$ rather than distributed along a chain, as in the adipate ion), both tests must be positive before one can safely conclude that Type II adsorption is operative.

A third type of adsorption (Type III) is that exhibited by such anions as NO_3^-, ClO_4^-, ClO_3^- and some others. These anions are known to be adsorbed on mercury[2-4] at the potential of the electrocapillary maximum (by the criteria mentioned under Type II adsorption), but it is almost inconceivable that they should form covalent bonds with mercury under these conditions. A more probable explanation was given many years ago by Frumkin, Reichstein and Kulvarskaja[7] in connection with their study of the adsorption of anions at an air–water interface. It was found that nitrate and perchlorate ions are adsorbed at an air–water interface (though not so strongly as at a mercury–solution interface) and it was pointed out that these ions, by virtue of their size, possess what we should nowadays call large structure-breaking tendencies. The latter effect can be seen, for example, by comparing the relative partial molal entropies of water in various solutions of 1:1 electrolytes.[8] Frank and Robinson say[8] "For the univalent electrolytes the maximum disturbing effect is shown by KNO_3. This might be attributed to the plane triangle structure of the nitrate ion and its inability to fit smoothly into the four coördinated structure of water." Although data for perchlorates are not available, we would predict an almost equally strong effect upon the relative partial molal entropy of water. It seems clear that nitrate and perchlorate ions at an interface are at a lower potential energy than ions in the interior of the solution because of the fewer hydrogen bonds broken by an ion in that location. The adsorption of nitrate ion on mercury is probably favored relative to its adsorption at an air–water interface by the effectively infinite dielectric constant of the metal, since this makes it possible for the ion to lose water of hydration on the side of the metal without a major loss of its energy of solvation.

It is convenient to say that these anions are squeezed out of solution, and the reality of the effect can hardly be doubted in the case of the adipate ion, for instance, where the hydrophobic part of the molecule unquestionably squeezes the ion to the interface.

A fourth type of adsorption is to be expected when one stops to consider the possibility of lateral interaction between ions which have been squeezed out of solution. It is well known that a monolayer of un-ionized molecules can form at an interface, and it is clear that in many cases lateral interaction (van der Waals forces) will help to stabilize the layer. The same type of interaction is to be expected with anions of long-chain organic acids and, when found, it will be called Type IV adsorption. Strictly speaking it is a sub-class of Type III adsorption, since anions which show strong lateral interaction would normally be expected to be of a type which would be squeezed out of solution also.

Experimental Details

The differential capacity measurements were carried out on an apparatus developed by one of us and described previously.[9] Some surface tension measurements also were made by the drop-time method, but better results could be obtained by integrating the differential capacity data twice

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[5] The most recent is that of J. R. Macdonald, *J. Chem. Phys.*, **25**, 364 (1956), which will serve as a key to the earlier literature.

[6] G. Gouy, *Compt. rend. acad. sci.*, **146**, 612 (1908).

[7] A. Frumkin, S. Reichstein and R. Kulvarskaja, *Kolloid Z.*, **40**, 9 (1926).

[8] H. S. Frank and A. L. Robinson, *J. Chem. Phys.*, **8**, 933 (1940).

[9] D. C. Grahame, THIS JOURNAL, **71**, 2975 (1949).

with respect to potential in cases where this procedure is allowed. However, the most interpretable data turn out to be capacity values themselves, and the present paper will be concerned with these.

Although the adsorption process *per se* is usually very fast in measurements of this kind, considerable time is needed for large molecules to diffuse to the surface. The extent to which diffusion equilibrium is attained can be estimated by taking measurements at different times on a stationary droplet or by taking measurements on a moving droplet whose rate of growth is subject to control. In a series of control experiments the rate of flow of the mercury was altered, keeping constant the size of the droplet at the moment of measurement. No significant variations of capacity attributable to the slow rate of diffusion of the adsorbate could be noted except at or near the potential of the desorption peaks of polymeric anions. An example of the observed behavior in such a case is shown in Fig. 1 which shows the diffusion lag to exert an appreciable effect on the measurements only in very dilute solutions of the adsorbate. To avoid this source of uncertainty, the measurements reported below deal only with solutions concentrated enough not to show this effect. The matter was very thoroughly checked over a wide range of conditions. For the purposes of the present paper, it does not matter greatly, however, since the capacity curves are to be used directly and not integrated. (It is the integrated curves which are most seriously in error if the diffusion is too slow.)

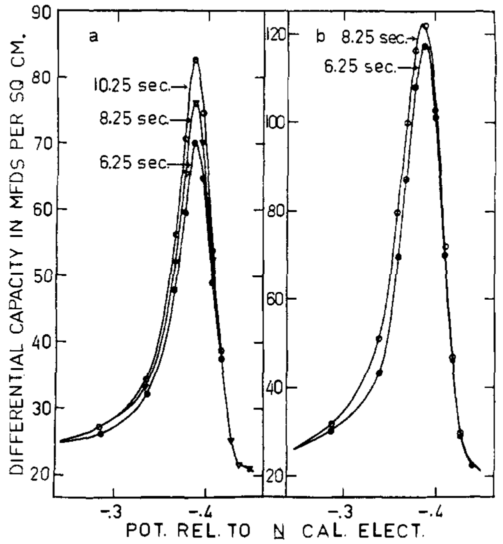

Fig. 1.—Differential capacity curves taken at same Hg drop size but different drop ages. Ionized PMA at 61°; z = 4500; supporting electrolyte, 0.1 N NaF + 0.001 N NaOH; concn. of PMA = 0.000125 N (a) or 0.00025 N (b).

Results and Conclusions

Dibasic and Tribasic Acids.—The sodium salts of oxalic, adipic, glutaric and 1,2,3-propanetricarboxylic acids were dissolved in a supporting electrolyte composed of 0.1 N NaF + 0.002 N NaOH. The supporting electrolyte was added as a means of ensuring that the results would be comparable to those obtained later using polymeric acids in solution. The principal results are shown in Fig. 2.

It will be observed that the anions of these acids raised the capacity in a characteristic manner, different for each. The approximate values of the potential of the electrocapillary maximum (e.c. max.) are marked with short vertical lines on the figures. It is at these potentials that the influence of the anion is most simply seen.

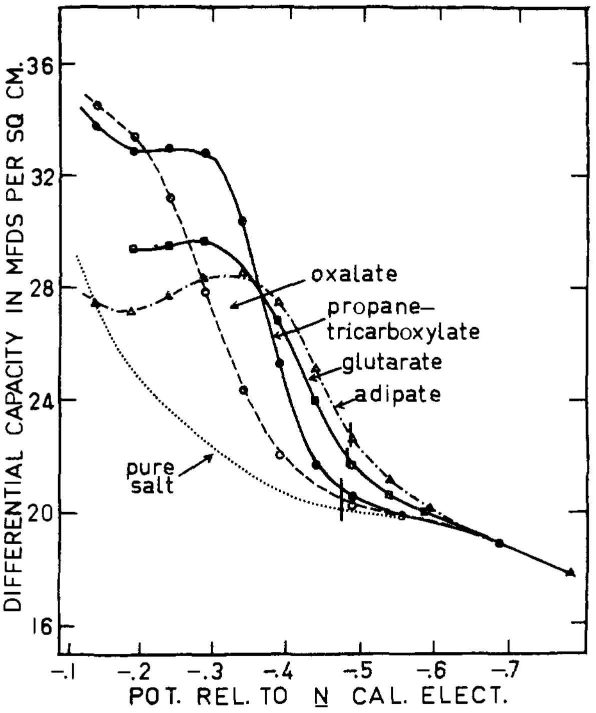

Fig. 2.—Differential capacity curves in presence of 0.06 N solutions of sodium salts as indicated. Supporting electrolyte, 0.1 N NaF + 0.002 N NaOH; t = 25°.

The oxalate ion raises the differential capacity of the double layer at the potential of the e.c.max. only very slightly, and its behavior is only a little different from that of the sulfate ion at all potentials (data not shown). From purely chemical considerations one would not expect either the sulfate or the oxalate ion to be chemisorbed even on positively charged mercury, and in spite of some conflicting evidence on this point with regard to the sulfate ion,[4] that is the assumption upon which we shall proceed to discuss further results.[10] Therefore the curve for the oxalate ion will be regarded as normal for a divalent anion with charges not much separated.

The glutarate ion, with three CH_2 links in the chain, would be expected to exhibit mild outsqueezing (Type III adsorption), and this is the presumed reason for the increased capacity (Fig. 2). It is usual for adsorption of an anion to increase the capacity of the double layer, no clear-cut exceptions to this rule being known, except as indicated below. The "hump" in the curve has been explained by one of us (D.C.G.)[11] as the result of the formation of a quasi-crystalline semirigid layer of solvent at the interface. A different interpretation relating to the orientation and re-orientation of the adsorbed molecules will be presented by the other author (I.R.M.) in a separate publication. In this paper we shall not defend either point of view.

The adipate ion, with four CH_2 groups, con-

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(10) It does not really matter in the ensuing discussion whether this assumption is strictly correct or not, and it greatly simplifies the presentation.

(11) D. C. Grahame, *J. Chem. Phys.*, **23**, 1725 (1955); THIS JOURNAL, **79**, 2093 (1957).

tinues the trend set by the glutarate ion and reinforces our explanation of it. It is interesting, then, to compare the behavior of the anion of 1,2,3-propanetricarboxylic acid. This can best be thought of as a glutarate ion with one H atom replaced by carboxylate. The marked change in the differential capacity curve shows two effects of increasing the charge on the ion. First, it suppresses the out-squeezing effect at the e.c.max. By increasing the energy of interaction of the ion with water, the ion is kept in solution, away from the interface. At more anodic potentials the capacity rises rapidly, and this is characteristic of an ion of multiple charge. In other words, Type I adsorption becomes dominant.

Although we do not have comparable data for the formate ion, it seems reasonable to suppose that its differential capacity curve on mercury under these conditions would resemble that of the pure salt shown as a dotted line in the figure. If so, the curves for formate, oxalate and propanetricarboxylate ions would illustrate well the effect of increasing the charge on an anion.[11a] (Cations show no such effect.)

Polyaspartic and Polyglutamic Acids.—The polymers used for this investigation were of relatively low molecular weight (degree of polymerization about 30). Their behavior is closer to that of the dibasic and tribasic acids than to that of the high molecular weight polymethacrylic acid (PMA). The repeating unit in polyaspartic acid is NHCH(CH_2COOH)CO which makes it roughly comparable to butyric or valeric acid. The relatively large number of hydrophobic groups per carboxylate ion accounts for the rather large capacity seen in Fig. 3 even at the potential of the e.c.max. This is strong Type III adsorption. Although each anion carries a total of about 30 negative charges, these are so uniformly distributed and so widely spaced along the chain that adsorption takes place even when the mercury surface is negatively charged, a somewhat noteworthy result.

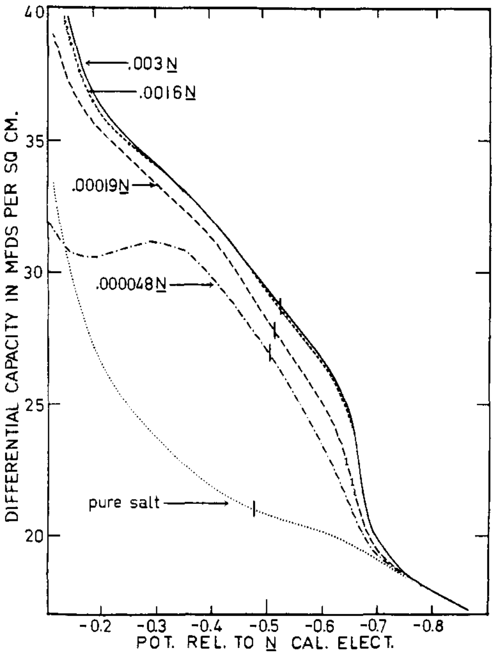

Fig. 3.—Differential capacity curves in presence of ionized polyaspartic acid. t = 25°; drop age = 30.25 sec.; concn. as indicated. Supporting electrolyte as in Fig. 2.

The data for the curve at 0.000048 N are reproduced as a matter of interest, but at this low concentration it would be unwise to disregard the effect of the low rate of diffusion of the adsorbate, which may lead to considerable error in the results.

The absence of a "hump" (except at the lowest concentration) should be pointed out, although no explanation will be offered at this point.

The anion of polyglutamic acid, with one more CH_2 group in the side chain, shows (in Fig. 4) the beginning of what we have called Type IV adsorption. At the highest concentration studied a peak appears in the capacity curves, and the height of the peak is strongly frequency dependent. These peaks are characteristic of adsorption–desorption phenomena of the type studied extensively in the past using un-ionized adsorbates.[12-14] The appearance of such peaks has always been associated with the formation of a monolayer, and this appears to be a reasonable explanation here also, except that in this instance the monolayer is probably incomplete as indicated by facts which will be explained presently. The layer will be called a monolayer in what follows to avoid cir-

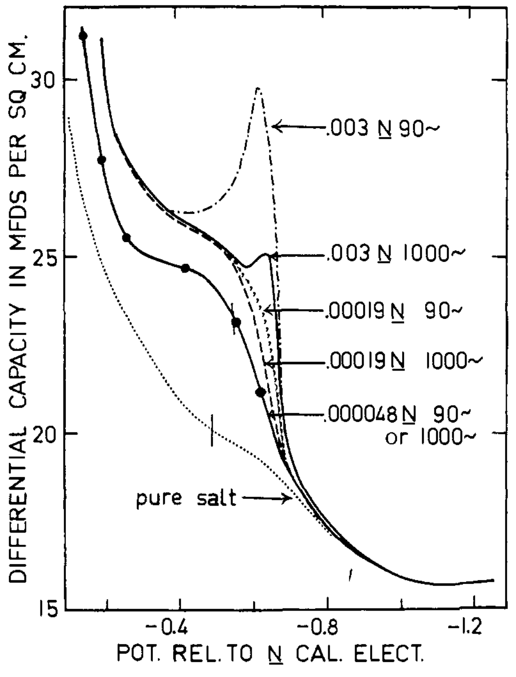

Fig. 4.—Differential capacity curves in presence of ionized polyglutamic acid. t = 25°; drop age = 30.25 sec.; freq. and concn. as indicated. Supporting electrolyte, 0.1 N NaF + 0.0015 N NaOH.

[11a] NOTE ADDED IN PROOF.—Strictly speaking one should compare the acetate, succinate, and tricarboxylate ions. The trend is the same as that shown in Fig. 2.

(12) M. A. Proskurnin and A. Frumkin, *Trans. Faraday Soc.*, **31**, 110 (1935).

(13) D. C. Grahame, *Chem. Revs.*, **41**, 441 (1947).

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

cumlocution. The significance of the peak in the capacity curve is that at the potential involved there is a sudden potential-dependent change in the composition of the double layer corresponding to the displacement of solvent by adsorbate. It is of interest that in Fig. 4 the peak occurs approximately at the potential of the e.c.max., which indicates, as one would expect, that a monolayer of anions does not form readily on a negatively charged surface even when the molecule has a considerable number of hydrophobic groups tending to put it there.

With non-electrolytes two desorption peaks are generally observed.[12] A second peak has not been observed in any of the work described in this paper, presumably because it is impossible to desorb a negatively charged ion from a positively charged surface by making the surface more positive.

In somewhat more dilute solutions of polyglutamic acid ($\sim$0.0002 N) there is a small dispersion of the capacity in the potential range where monolayer formation tends to occur (Fig. 4). Probably this signifies the formation of "patches" or "islands" of adsorbate at the interface, covering perhaps 10% of the metallic surface. In still more dilute solutions the dispersion vanishes, as one would expect according to this explanation.

Polymethacrylic Acid.—Three polymers of polymethacrylic acid (PMA) were used, and these were fractionated to samples having average degrees of polymerization z of 1950, 2600 and 4500 with a half-band width of approximately 7%.[15] Differential capacity curves obtained with fully ionized samples of the polymer for which z = 1950 are shown in Fig. 5.

A resemblance to the behavior of polyglutamic acid is evident, but the phenomena are now exaggerated to such an extent that their interpretation would be difficult if one did not have the former results as a guide. What is seen is an adsorption–desorption peak of great height and shifted in potential toward the anodic part of the curve. The rise in the capacity starts very suddenly at a potential which is either equal to or a little anodic to that of the e.c.max. To the left of the peak there is undoubtedly a surface layer of anions (analogous to the surface layer of polymethacrylic acid reported earlier[16]). The low value of the capacity in this state is attributed to the fact that once a monolayer of anions is formed, further increase in the concentration of anions occurs only slowly. Since the capacity was not abnormally low under similar conditions in Fig. 4, it was assumed that monolayer formation was incomplete, as stated above.

It is of interest that the results shown in Fig. 5 are frequency independent and occur at low temperatures (0°) as well as at higher temperatures, where the results (not shown) are not qualitatively different except that at higher temperatures (*i.e.*, 61°) the peak is about 20% higher than at 0°. The frequency independence indicates that whatever reorientation of molecules or bonds is needed for the formation of the adsorbed layer does not involve a significant activation energy. This fact is in agreement with the observation that the height of the peak is not strongly temperature dependent. A rather more complicated situation exists with un-ionized PMA, where the height of the peak is strongly temperature dependent and only in certain cases frequency dependent.[16] The difference is almost surely attributable to the well known dependence of configuration upon degree of ionization, the anion being relatively uncoiled. This uncoiling presumably involves the breaking of hydrogen bonds, which leaves the ion free to adsorb without further breaking of such bonds.

Samples of ionized PMA of higher molecular weight were indistinguishable in their behavior from the results here presented. The same result was also observed with un-ionized PMA and is attributed as before[16] to the fact that diffusion of whole molecules plays a negligible role. Those molecules which were able to reach the surface in the eight or ten seconds during which the mercury droplet was being formed in the solution gave rise to the observed results; the rest played no part.

The surface area per structural unit of the polymer can be computed as follows. At a potential somewhat to the left of the peak (say +0.180 v., relative to the e.c. max.) the total surface charge density is about 12 μcoul./cm.^{2} or 12 $\times$ 10^{-11} monomoles/cm.^{2}. This is 7.2 $\times$ 10^{13} structural units per sq. cm., hence each unit covers an area of 140 Å.^{2}, which seems reasonable, although somewhat larger than might have been guessed. This calculation is rough, since it disregards the fact that a part of the observed charge could be fluoride ion. If so, the area covered by each structural unit of the PMA would be even larger than 140 Å.^{2}, which seems so unlikely that we tend to believe that the ions of the PMA expel the fluoride ions almost completely. Also it seems likely that because of the outsqueezing effect, ions such as those from PMA will have a large inherent advantage over fluoride ions in their competition for space at the positively charged mercury surface.

Adsorption of PMA at Various Degrees of Ionization.—The electrocapillary behavior of PMA in the ionized state is entirely different from its behavior in the un-ionized state. It is to be expected that the properties of partly ionized PMA will stand in between those of the ionized and un-ionized polyelectrolyte. In Fig. 6 differential capacity curves at four different degrees of ionization are shown. From the figure it is clear that the height and sharpness of the peak diminish as the degree of ionization diminishes and the potential at which the rise starts to occur also becomes more cathodic. At α = 0.5 traces of another peak are perceptible at a potential of about -0.7 volt. At α = 0.16 this peak is much more pronounced and

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[15] The approximate degree of polymerization of the PMA before fractionation was 4000. From this mixed polymer 14 fractions were obtained in a range of z-values from 500 to 5500. The degree of polymerization of the different fractions was obtained by light scattering measurements in a 90° turbidimeter coupled with a Pulfrich visual split-field photometer and also by viscosity measurements in an Ostwald-Fenske viscosimeter where the PMA was present first in 2 N NaOH and then in 0.002 N HCl. The results were interpreted by means of Figs. 6 and 7 of A. Katchalsky and H. Eisenberg, *J. Polymer Sci.*, **6**, 145 (1951). The mean half width of z was estimated from the differences in the z's as determined by the three methods.

[16] I. R. Miller and D. C. Grahame, THIS JOURNAL, **78**, 3577 (1956).

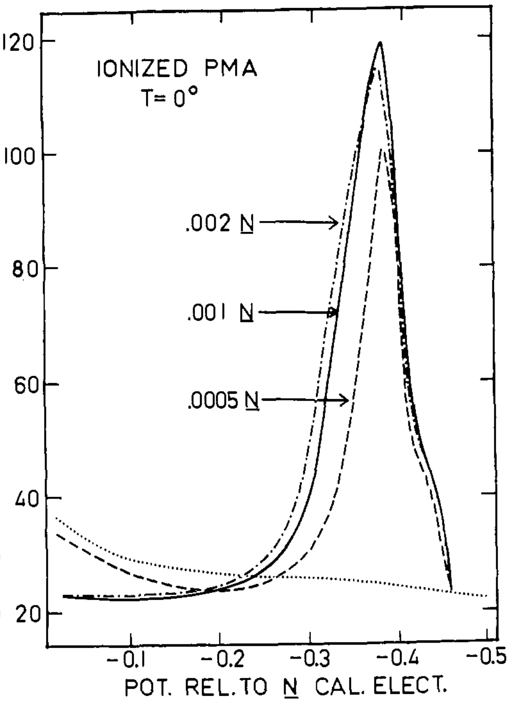

Fig. 5.—Differential capacity curves in presence of ionized polymethacrylic acid (PMA). $t = 0°$; $z = 1950$; freq. = 1000 cycles; concn. as indicated; supporting electrolyte as in Fig. 2.

has moved to a more negative potential. Nevertheless, the potential of this peak is more positive than the corresponding desorption potential of un-ionized PMA. The shift in the potential of the peak with the degree of ionization recalls the similar behavior of the peaks which are seen in the presence of monomeric substances at various concentrations (*cf.* behavior of butyric acid in paper I[15] or of aliphatic alcohols in the work of Melik-Gaikazyan[14]). In paper I attention was called to the fact that the desorption potential in the presence of un-ionized PMA does not depend upon the concentration of the polymer. The given reason for this behavior was the assumed constant concentration of polymer segments in the adjacent layers (called the surface phase) to the adsorption layer. This concentration was assumed to be close to the segment concentration in the polymeric coil. By ionizing part of the carboxylic groups and by diluting the surface phase as a consequence of electrostatic repulsion, which increases with the degree of ionization, the over-all concentration of the un-ionized groups in the surface phase decreases. Thus in this respect increased ionization of a polyelectrolyte is analogous to decreased bulk concentration of a monomeric surface-active substance.

The analogy just drawn is not complete, however, because each un-ionized segment of the chain is terminated by two ionized segments, and these inhibit and tend to prevent the adsorption of the un-ionized segments on the negatively charged surface. For this reason the change with concentration of the potential of the peak shifts in the opposite direction from that of un-ionized monomeric substances.

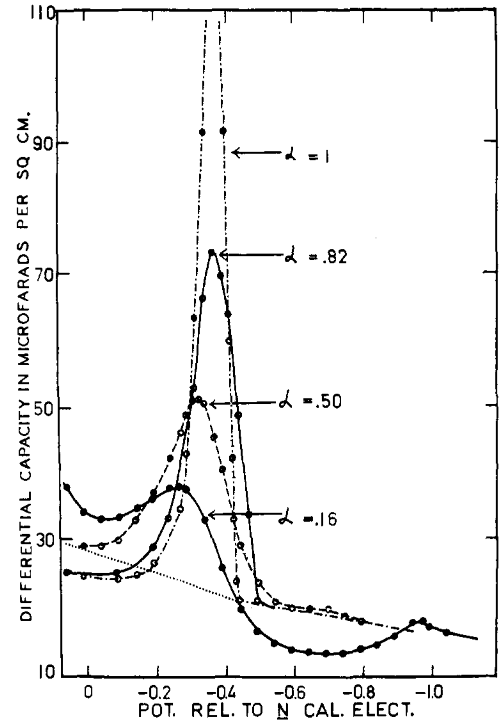

Fig. 6.—Differential capacity curves in presence of partially ionized PMA. When $\alpha = 1$, *p*H 11; $\alpha = 0.82$, *p*H 6.85; $\alpha = 0.50$, *p*H 5.7; $\alpha = 0.16$, *p*H 4.7. Supporting electrolyte = 0.1 *N* NaF + NaOH as needed to produce desired *p*H. $t = 25°$; $z = 1450$.

Copolymers of Methacrylic Acid with Methyl Methacrylate.—The degree of dissociation in the surface is not necessarily the same as the degree of dissociation of the same substance in the bulk

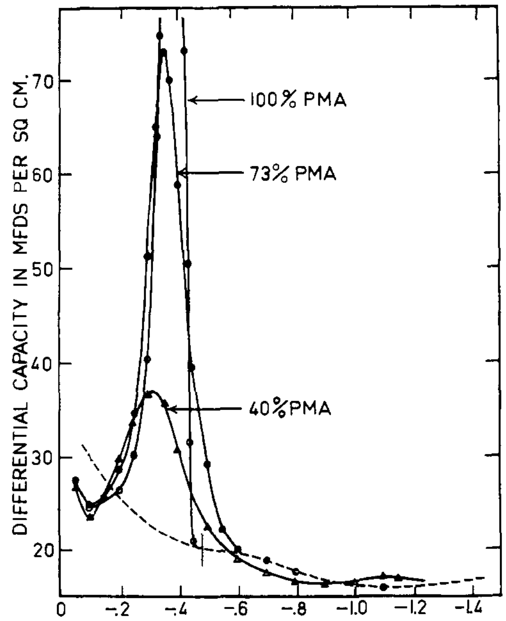

Fig. 7.—Differential capacity curves in presence of copolymers of methacrylic acid and methylmethacrylic acid in different ratios. $t = 25°$; composition of polymers as indicated; supporting electrolyte as in Fig. 2.

phase. Differences may arise from the tendency of protons to be attracted toward or repelled from the charged surface, and indeed it was apparent in paper I[15] that undissociated PMA undergoes partial dissociation at a positively charged surface. Another way of looking at the matter is to say that conditions at the interface are so different from those in the interior of the solution that one could hardly expect to find the same values of K_a there if K_a is expressed in terms of the *concentrations* of the species concerned.

In order to be more sure about the extent of ionization at the interface, copolymers of methacrylic acid with methyl methacrylate were prepared and studied. At sufficiently high *p*H values there is no doubt that these copolymers are fully ionized and that the number of ionized groups for a given length of chain depends merely upon the methacrylic acid content of the polymer. Figure 7 shows the results obtained in this way with two copolymers. The peaks occur at the same potentials, and their heights are about what one would expect if the degree of ionization shown in Fig. 6 (computed from the *p*H) is correct. The striking similarity of the two figures indicates that the degree of ionization in the interior of the solution is close to the degree of ionization at the interface.

At sufficiently anodic potentials (below −0.23 v.) the capacity values are almost independent of composition in the case of the two copolymers. The significance of this fact, and also of the sudden upturn at the left-hand end of the two curves, remains in doubt. The polymers of methacrylic acid (Fig. 6) do not show this behavior but exhibit the expected properties on anodic polarization. Thus the fully ionized material shows the lowest capacity and not much turning up, whereas the less fully ionized samples show a larger capacity and an upturn at the end corresponding to the phenomenon of induced ionization discussed in part I.[15]

Summing up, we find that it is usually possible to interpret the differential capacity curves of PMA, both ionized and un-ionized, obtained at a mercury–solution interface and that the results are in accord with previously held views concerning the structure of the double layer.

Acknowledgment.—The authors are indebted to the U. S. Office of Naval Research for the support of this work. One of the authors (I.R.M.) wishes to express his thanks to Professor A. Katchalsky for helpful discussions.

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Anomalous Optical Rotations of Coördination Compounds[1]

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RECEIVED FEBRUARY 9, 1957

The previously reported change in sign of optical rotation of *d-cis*-$[Co(en)_2Cl_2]Cl$ with a change in concentration is not observed if the light used is monochromatic. Results are compared using a sodium lamp, white light filtered through colored glass filters, and white light filtered through an interference filter plus colored glass filters. The effectiveness of the filter combinations in removing all but the NaD doublet from the spectrum produced by the sodium lamp are compared. A change in magnitude but not in sign of optical rotation was noted for K[Co(edta)] using different light sources.

It is well known that the specific rotations of highly colored coördination compounds can change with wave length of light from large negative values to large positive values. Differences in magnitude or even in sign of rotation also have been reported for solutions of the same complex at the same wave length for different concentrations. The specific rotation of a 0.4% solution of *d-cis*-$[Co(en)_2Cl_2]Cl$ was reported to be −200° and that of a 0.1% solution +215°.[2] Such results have led to expressions of caution that concentrations should be reported in addition to the wave length of light used.[3]

The difficulties have arisen because of the need to increase the light intensity for densely colored solutions and this has been accomplished at the expense of spectral purity. The sodium lamp, with an orange cut-off filter to eliminate any light of shorter wave length, is commonly used as the source of the NaD doublet. For densely colored coördination compounds a more intense source has been obtained by using various filter combinations which give very broad bands of transmitted light.

The purpose of this investigation was to study the change in sign of rotation with change in concentration and to determine the limits of usefulness of several light sources or filter combinations.

Experimental

The *d-cis*-$[Co(en)_2Cl_2]Cl$ was prepared and resolved by the method described by Bailar.[2] The directions refer to the compound as the *levo* form, but the rotation is actually positive at all concentrations for NaD light. The negative rotations are erroneous. The *d*-K[Co(edta)] (edta represents the ethylenediaminetetraacetate ion) was generously provided by Professor Francis P. Dwyer of the University of Sydney. The *d* prefix refers to the rotation of +1000° at 5461 Å.

Optical rotations were obtained with a Rudolph Model 70 Polarimeter. The readings for 0.3 and 0.4% solutions of *cis*-$[Co(en)_2Cl_2]Cl$ using the sodium lamp were obtained using a photoelectric attachment built by W. C. Erdman. All measurements were made at room temperature (25–30°) immediately after mixing the solutions.

The spectra of the sodium lamp with various filters were obtained with a Hilger constant deviation glass prism spectrograph. The transmission curves for the filters and solu-

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[1] This work was supported by a grant from the Research Corporation. Presented at the 130th Meeting of the American Chemical Society in Atlantic City, New Jersey, September 19, 1956.

[2] J. C. Bailar, Jr., *Inorg. Syn.*, **II**, 224 (1946).

[3] W. C. Fernelius, *Advances in Chem.*, **8**, 9 (1953).