Surface Chemistry of High Polymers. IV. The Monolayer of Polymethacrylic Acid and its Copolymers with Diethylaminoethyl Vinyl Ether at the Air/Water Interface

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As mentioned in the previous paper, there are some investigations on the film of non-electrolytic synthetic polymers.[1-5] There is, however, only a little investigation on that of synthetic polyelectrolytes.[6,7] The investigation of the latter film has many interesting points not only as the pure physical chemistry but also as an important model of biocolloidal substances, as pointed out by Katchalsky.[8] For these reasons, we studied first the monolayer of polymethacrylic acid (PMA) and its copolymers with diethylaminoethyl vinyl ether (DAV) at the air/water interface, and investigated how the ionization of these polymers affects their behaviour at the interface. The results obtained will be described in the present paper. The result at the oil/water interface will be published later.

Experimental

The polymers used in the present investigation

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[1] T. Isemura, H. Hotta and T. Miwa, This Bulletin, **26**, 380 (1953).

[2] H. Hotta, This Bulletin, **26**, 386 (1953).

[3] H. Hotta, This Bulletin, **27**, 80 (1954).

[4] T. Isemura and K. Hamaguchi, This Bulletin, **25**, 40 (1952); **26**, 425 (1953).

[5] D. J. Crisp, *J. Colloid Sci.*, **1**, 49 and 161 (1946).

[6] T. Isemura and K. Hamaguchi, to be published in This Bulletin.

[7] A. J. G. Allen and A. E. Alexander, *Trans. Faraday Soc.*, **46**, 316 (1950).

[8] A. Katchalsky, *J. Polymer Sci.*, **7**, 393 (1951).

were prepared as follows. Polymethacrylic acid (sample M) was prepared by the usual method. Copolymers of methacrylic acid (MA) and diethylaminoethyl vineyl ther ($(C_2H_5)_2$-N-C_2H_4-O-CH $=CH_2$) (DAV) were prepared by two different methods. Sample L was copolymerized from an equimolar mixture of MA and DAV dissolved in 60% aqueous methanol solution, using potassium persulphate as catalyst (0.2 mole percentage). On the other hand, sample K was copolymerized from an equimolar mixture of MA and DAV dissolved in N/2 hydrochloric acid, using potassium persulphate as catalyst (0.1 mole percentage), and obtained as hydrochloric acid salt. The composition of these copolymers, which was estimated by nitrogen analysis, is shown in Table I with the mean molecular weight per vinyl unit. The details of the copolymerization and the properties in the bulk phase of these copolymers will be reported elsewhere.

TABLE I
THE COMPOSITION OF COPOLYMERS OF METHACRYLIC ACID (MA) AND DIETHYLAMINOETHYL VINYL ETHER (DAV).

Sample	Mole percentage of DAV in copolymer	Mean molecular weight per vinyl unit
K	31	112
L	20	97
M	0	86

We measured their surface pressure by the hanging plate method, and their surface potential by the vibrating electrode method at room temperature (10–15°C.). The apparatus and procedure for these measurements were almost the same in the previous paper[1] except some modification for the development of accuracy. The film was spread from aqueous 20% pyridine solution on the aqueous phase at various pH, which was controlled with hydrochloric acid or sodium hydroxide, and determined by "TOYO" test paper.

Results

The surface pressure-area curves and surface potential (or surface moment)-area curves on the aqueous phase at various pH are shown in Figs. 1, 2 and 3, and in Figs. 4, 5 and 6, respectively. Although the surface potential-area curves for sample K at pH 5.8, 8.0 and 12.1 were not entirely identical with curve in Fig. 4, they were not essentially different from it. The surface moment-area curves, shown by dotted lines in the figures, were calculated by the usual method as mentioned in the previous paper.[1] The surface moment of all samples at the constant range obtained was plotted against the pH of aqueous phase in Fig. 7 to clarify the relation between them. The points under the ground line of surface moment in this figure correspond to the negative as curve e in Figs. 4 and 6. In these figures, the area was calculated as the mean area per vinyl unit with the mean molecular weight in Table I.

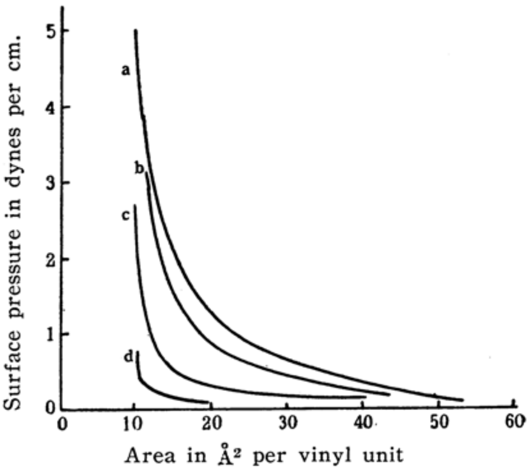

Fig. 1. The surface pressure-area curves of samle K on various pH. Curve a (pH 1.4); curve b (pH 2.4); curve c (pH 3.9); and curve d (pH 4.4)

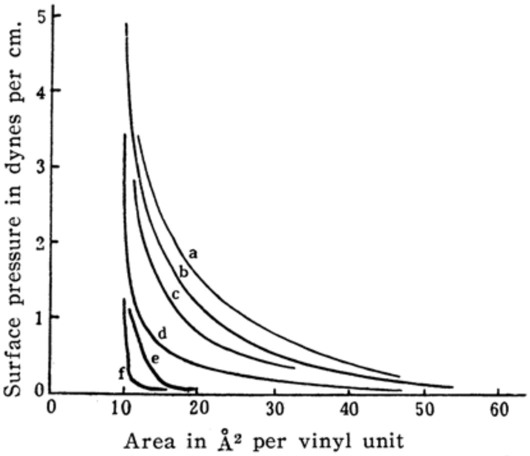

Fig. 2. The surface pressure-area curves of sample L on various pH. Curve a (pH 1.0); curve b (pH 1.4); curve c (pH 2.6); curve d (pH 3.8); curve e (pH 4.9); and curve f (pH 5.3)

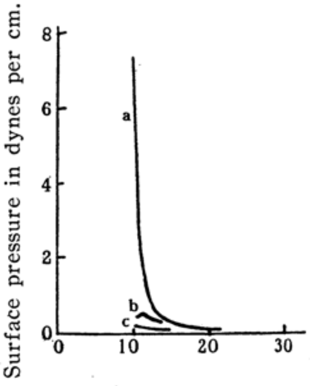

Fig. 3. The surface pressure-area curves of polymethaerylic acid (sample M) on various pH. Curve a (pH 1.6, 3.4, 4.0, and 4.4); curve b (pH 4.7); and curve c (pH 7.5)

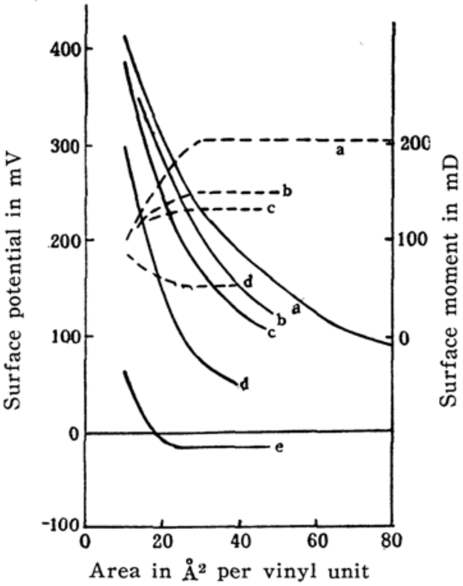

Fig. 4. The surface potential (or surface moment)- area curves of sample K on various pH. The surface moment is shown by dotted line. Curve a (pH 1.0, 1.4, 2.6, and 3.8); curve b (pH 4.5); curve c (pH 4.8); curve d (pH 5.3); and curve e (pH 5.8, 8.0 and 12.1)

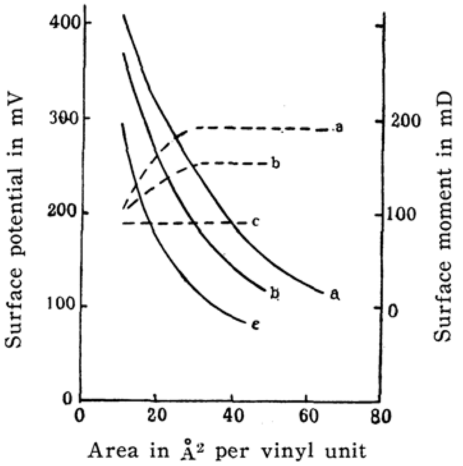

Fig. 5. The surface potential- (or surface moment)- area curves of sample L on various pH. The surface moment is shown by a dotted line. Curve a (pH 1.4, 2.4, and 3.8); curve b (pH 4.4); and curve c (pH 4.9)

Discussion

Since even the interpretation of the properties of the solution of linear polyelectrolyte is a subject recently developed, its theory at the interface is scarcely established at present. However, since there are some exact investigations on the solution of polymethacrylic acid as the representative of linear polyelectrolytes, we shall consider the present result of monolayer in comparison with the knowledge of the behaviour of this polyelectrolyte in the bulk phase.

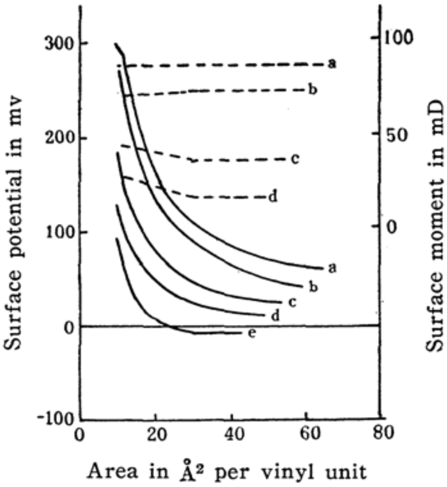

Fig. 6. The surface potential- (or surface moment)- area curves of polymethacrylic acid (sample M) on various pH. The surface moment is shown by a dotted line. Curve a (pH 1.6, 3.4 and 4.0); Curve b (pH 4.4); Curve c (pH 4.7); Curve d (pH 5.3); and Curve e (pH 7.5)

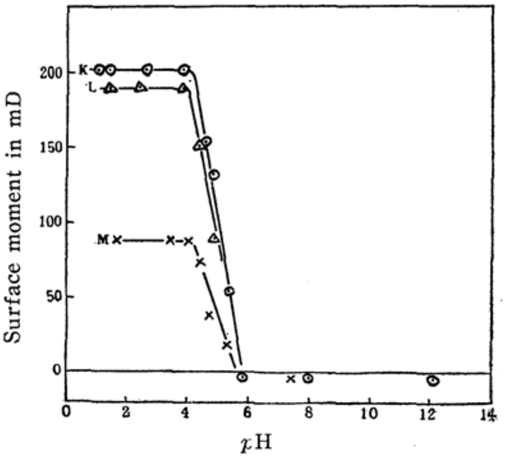

Fig. 7. The relation between surface moment and the pH of substrate. Sample K (⊙), L (△), and M (×), respectively

The Monolayer of Polymethacrylic Acid (PMA) (sample M)—It is evident from Figs. 3, 6 and 7 that the surface pressure and surface moment of PMA were completely identical up to nearly pH 4.0, and fell rapidly down to zero between pH 4.0 and 5.5, and the surface potential became even negative at pH greater than 5.5. This trend of change of the surface behaviours with pH corres-

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9) A. Katchalsky, O. Künzle and W. Kuhn, *J. Polymer Sci.*, **5**, 283 (1590).

ponds entirely to the properties of the bulk solution of PMA, which were interpreted in detail by Katchalsky.[8,9] It is found as mentioned below that the former is also perfectly understood by his interpretation of the relationships between the state of molecules and the degree of ionization of polyelectrolyte in solution[8].

Since the molecules are rigid and not affected by ionization at a low degree of ionization up to *p*H 4.0 in consideration of his interpretation, the surface pressure and surface moment are entirely unchanged by *p*H, and then, since they open up with increasing ionization and take the form of freely kinked threads up to about 10% ionization (*p*H 5), the surface moment is lowered due to the negative charge of carboxyl groups, and, since the spreading molecules begin to dissolve into the aqueous phase due to their stretching with more increasing ionization, the apparent surface pressure and surface moment are more and more decreased. Finally, since the molecules can no more stand at the interface in the same form as that in the aqueous phase, namely, in the form of rodlike filaments at the higher degree of ionization, the greater part of spreading molecules tends to take the further stable form and therefore dissolves into the aqueous phase as shown as curve e in Fig. 6. That is, the difference of energy between the forms of molecules at the interface and in the aqueous phase rapidly increases with the increase of degree of ionization.

The Monolayer of Copolymers with DAV (sample K and L)—From Figs. 1, 2, 4, 5 and 7, it can be recognized that the surface pressure and surface moment of both copolymers at the same *p*H were almost the same, in spite of their different compoistion, while the surface pressure increased with decreasing *p*H. The change with *p*H was exactly parallel to that of PMA over all *p*H range investigated.

Before discussing these phenomena, it may be considered how the side chains of the present copolymers orientate at the interface. It was concluded from the surface pressure and surface moment in the preceding paper[3] that the carboxyl groups of PMA are immersed in the aqueous phase. Furthermore, diethylaminoethyl groups may also be immersed in the aqueous phase for the following reasons. (I) Triethylamine, which resembles this group, is appreciably soluble in water. (II) The shape of surface pressure-area curves of the present copolymers are independent of their composition and similar to that of PMA, in the condensed state at low ionization, in contrast with the copolymers of vinyl acetate and stearate,[1] and do not show any kink point which should appear if the side chains lie flat in the interface. (III) Their surface potential is very regular and reproducible in contrast with the copolymers of vinyl acetate and stearate.[1] Therefore, the discussion of the behaviour of the monolayer of these polymers in the light of the effect of ionization and without any consideration of the steric effect of side chains causes no serious error in this case.

Subsequently, we notice the phenomenon up to *p*H 4.0 from *p*H 1.0. In this *p*H range, the amine groups may be completely dissociated in accordance with their fraction in the polyelectrolytes and the dissociation constant of monomer. However, as shown in Fig. 7, the surface moment of both copolymers is nearly equal in spite of their different composition. When we evaluate the surface moment of dissociated amine groups, on the assumption of their perfect dissociation and of the perfect undissociation of carboxyl groups of methacrylic acid, of which the surface moment was found to be 88 mD from curve M in Fig. 7, we found the surface moment of ionized amine groups is 450 mD for sample K and 600 mD for sample L, respectively. On the other hand, the surface moment of $C_{18}H_{37}N(CH_3)_3^+$ was reported to be 600 mD or more.[10] From these facts, it is concluded that the amine groups of both copolymers are almost equally dissociated by about 20%,[1] and the remainder of amine groups are not dissociated and have the surface moment nearly equal to that of undissociated PMA (90 mD). It is also understood on the same basis that the surface pressure of these copolymers at the same *p*H was almost identical as shown in Figs. 1 and 2 in spite of their different composition.

The dissociation of amine groups is imperfect because the condensation of film, due to the action of hydrogen bonds operative between the undissociated carboxyl groups of MA, makes them too close for their perfect ionization. The film is, of course, expanded in nature, but seems to be still fairly condensed even at *p*H 1.4 in comparison with the result at the oil/water interface which will be published in the following paper. It is also explained by considering the relation between the shape of the molecule and the degree of ionization interpreted by Katchalsky.[8]

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[10] J. T. Davies, *Proc. Roy. Soc.*, (London), **208** A, 224 (1951).

[11] The total ionizable groups, namely, the sum of MA and DAV is taken hereafter as the standard of the degree of ionization.

From all the figures we notice that the surface moment-area curves are bent at about 30 Å², and approach to about 90 mD at about 10 Å², in Fig. 5 shows the surface moment of 90 mD, and has no bending point. This tendency is shown not only in the case of the present copolymers, but also in that of PMA in Fig. 6. However, it does not show such a bending point in the undissociated or slightly dissociated state of PMA as shown in curve a and b in Fig. 6. From these facts, it is also concluded that the too close approaching of ionizable groups hinders the ionization due to the same mechanism as mentioned above and the above assumption, that the value of surface moment of undissociated amine groups may be 90 mD, is confirmed here. McBain and Peaker had already suggested the idea that the film of stearic acid can not be so much ionized in the solid state.[12] This is also related to the phenomenon that the conductivity of soap solution falls rapidly down with increasing concentration from the critical micelle concentration.[13]

Although the constancy of surface moment in this *p*H range in Fig. 7 appears at first sight to be contradictory to the fact that the surface pressure increases with decreasing *p*H as in Figs. 1 and 2, it is understood on considering that the surface pressure is more sensitive to the degree of ionization than the surface moment. The similar fact was already been pointed out in the previous paper.[14,15]

As mentioned above, the carboxyl groups of MA begin to dissociate appreciably from *p*H 4.0 with increasing *p*H. Consequently, since the positivity of the whole molecule decreases, the mean apparent surface moment gradually decreases. Since the effective charge density for the mutual repulsion of molecules is gradually decreased, the film is condensed. Therefore, the surface pressure-area curve at *p*H 4.9 (see Fig. 2) becomes similar to that of undissociated PMA (see Fig. 3), and the corresponding surface moment-area curve (curve c in Fig. 5) does not show a bending point as mentioned above. This fact is understood on assuming that the degrees of ionization of respective constituents, namely, MA and DAV balance each other at this *p*H, and therefore the molecule has essentially no charge as a whole. This *p*H is the surface isoelectric point of this copolymer. This is considerably less than that expected from the dissociation constant of both monomers and the composition of copolymer. It may be caused by the following facts. Since the molecules are condensed more strongly at the interface due to the larger content of MA than in the solution, the amine groups can not dissociate, due to too closely approaching at the interface, as much as in the solution.

With the further increase of *p*H, MA of the greater part of the copolymer is more and more ionized and then the molecules tend to stretch to rodlike form. Therefore, since the molecules can not stand in the stable form at the interface, they dissolve into the aqueous phase as mentioned in the section of PMA. It is because of the great content of MA in comparison with DAV that we could not obtain the stable film due to undissociated DAV at the higher *p*H as we could at the low *p*H.

Summary

As the result of the measurements of the surface pressure and surface potential of polymethacrylic acid and its copolymers with diethylaminoethyl vinyl ether on the aqueous phase at various *p*H, their surface moment was constant up to *p*H 4.0, then rapidly fell down to zero between *p*H 4.0 and 5.5, and finally their stable film could not be found at the higher *p*H range than 5.5, but the surface pressure decreased with increasing *p*H even up to *p*H 4.0. These tendencies are discussed in the light of Katchalsky's interpretation in regard to the relation between the shape of molecules and the degree of ionization.

The important conclusions from the present experiments are:

(1) all the side chains of the present polymer are immersed in the aqueous phase;
(2) the degree of ionization of amine groups may be of about 20% even at its maximum; and
(3) the isoelectric point of the present copolymer at the interface exists at about *p*H 5.0 of the aqueous phase.

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[12] J. W. McBain and C. R. Peaken, *Proc. Roy. Soc.*, (London), **125** A, 394 (1929).
[13] J. W. McBain, "Colloid Science", Chap. 17 (1950).
[14] H. Hotta and T. Isemura, This Bulletin, **25**, 101 (1952).
[15] A. E. Alexander, *Trans. Faraday Soc.*, **37**, 15 (1941).