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

By Hiroshi HOTTA

(Received March 22, 1954)

Previously we studied the monolayer of polymethacrylic acid and its copolymers with diethylaminoethyl vinyl ether at the air/water interface by measuring their surface pressure and potential.[1] Subsequently, we have studied the monolayer of the same samples at the petroleum ether/water interface. The results will be described in the present paper. The effect of the *p*H of substrate on the surface behaviour of polyelectrolyte can be perfectly inferred by comparison between the results at both interfaces. The present investigation provides an useful key to elucidate the nature of the biocolloidal substances.

Experimental

The polymethacrylic acid and its copolymers with diethylaminoethyl vinyl ether ($CH_2=CH-O-C_2H_4-N-(C_2H_5)_2$) (DAV) used in the present study were the same samples as those used in the preceding investigation,[1] and had the composition shown in Table I. Their films were spread from the aqueous solution containing 20% pyridine at the petroleum ether/water interface, using a micrometer syringe according to Alexander and Teorell's method.[2] The *p*H of substrate was adjusted with hydrochloric acid or sodium hydroxide, and measured with "TOYO" *p*H test paper. The occasional test of this value checked by the Beckman glass electrode *p*H meter agreed satisfactorily with each other. The interfacial pressure was measured by ring method,[3] and the interfacial potential by vibrating electrode method using the same apparatus as that described in the previous paper.[4] Detailed descriptions of the spreading technique and of the measurement of interfacial pressure were given in the previous paper.[5] The application of the vibrating electrode method to the measurement of interfacial potential at the oil/water interface has been already tried by Davies.[6, 7] Although the vibrating electrode was immersed in the petroleum ether phase, we took care sufficiently of the amplitude of vibration and the distance of the electrode from the interface not to disturb the film.

TABLE I

THE COMPOSITION OF COPOLYMERS OF METHACRYLIC ACID (MA) WITH 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

Results

The interfacial pressure (π)-area (A) curves and interfacial potential-area curves at the petroleum ether/aqueous phase at various *p*H interfaces are shown in Figs. 1, 2 and 3, and Figs. 6 and 7, respectively. In these figures, the area was calculated as the mean

---

[1] T. Isemura, H. Hotta and S. Otsuka, This Bulletin, **27**, 93 (1954).

[2] A. E. Alexander and T. Teorell, *Trans. Faraday Soc.*, **35**, 727 (1939).

[3] A. E. Alexander, "Surface Chemistry" (Supplement of Research) (1949) p. 123.

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

[5] H. Hotta, ibid. **26**, 386 (1953).

[6] J. T. Davies, *Nature*, **167**, 193 (1951).

[7] J. T. Davies, *Z. Elektrochem.*, **55**, 559 (1951).

area per vinyl unit with the mean molecular weight in Table I. The interfacial moment-area curves, shown by dotted lines in Figs. 6 and 7, were calculated by the usual method as mentioned in the previous paper.[4] Since the measurements of interfacial pressure and potential were carried out separately at room temperature for the reasons of apparatus, the temperature for the two curves was not the same, namely, 17-22°C. for interfacial pressure and 8-11°C. for interfacial potential.

The results for all samples were sufficiently reproducible up to *p*H about 4. On the other hand, the reproduciblity was good for sample K, fairly good for sample L, but somewhat uncertain for sample M in the *p*H range, in which carboxyl groups might be ionized. Therefore, the area in figures is the apparent mean area calculated mathematically in this *p*H range. Uncertainty increases somewhat in the narrower area range. The interfacial potential-area curve for sample M is given only in the case of *p*H 1.6 as a representative in Fig. 7.

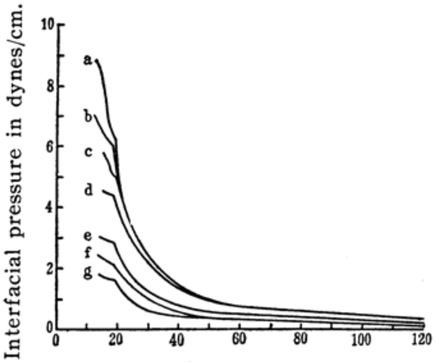

Fig. 1. The interfacial pressure-area curves of sample K at the various *p*H of substrate: curve a, *p*H 1.2; curve b, *p*H 2.8; curve c, *p*H 3.2; curve d, *p*H 3.5; curve e, *p*H 4.0; curve f, *p*H 4.8; and curve g, *p*H 5.7.

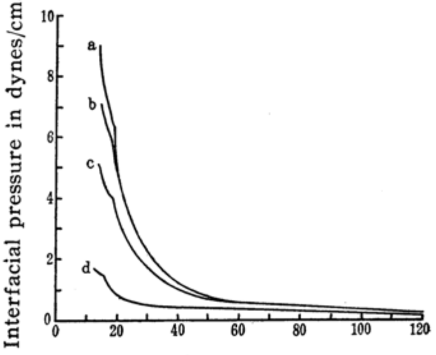

Fig. 2. The interfacial pressure-area curves of sample L at the various *p*H of substrate: curve a, *p*H 1.6; curve b, *p*H 2.6; curve c, *p*H 3.5; and curve d, *p*H 5.8.

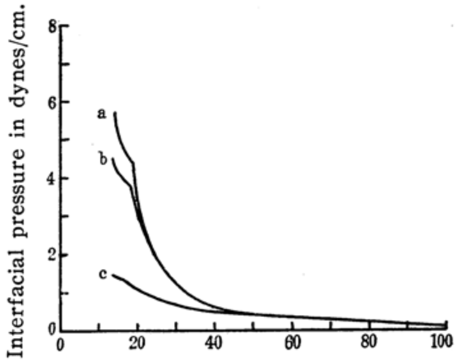

Fig. 3. The interfacial pressure-area curves of sample M at the various *p*H of substrate; curve a, *p*H 1.6; curve b, *p*H 3.0; and curve c, *p*H 3.5.

Discussion

It was concluded from the measurement of surface potential in the preceding paper[1] that, at the air/water interface, the amine groups of the present polyelectrolytes can be ionized by about 20 mol. per cent[8] at the maximum, and that the behaviour of their film can be perfectly understood by Katchalsky's interpretation[9] for the relationship between the state of a molecule and the degree of ionization (or *p*H). In view of the present results, our conclusion was still confirmed.

The film of the present polyelectrolytes is of expanded type as in the case of all other synthetic linear polymers at the oil/water interface[5, 10] as shown in Figs. 1, 2 and 3. The value of $(\pi A)_{A=\infty}$ and the collapse pressure (the interfacial pressure at a kink point) from these figures are plotted against the *p*H of substrate in Figs. 4 and 5, respectively. On comparing these figures with the curve of surface moment against the *p*H of substrate (Fig. 7 in the preceding paper[1]), we noticed that all the curves in these figures are constant up to a certain (and almost same) *p*H, and bend sharply from this *p*H. This tendency might be interpreted as in the case of the air/water interface.[1] That is, up to this critical *p*H the acid groups may be perfectly undissociated and

---

[8] The total ionizable group, namely, the sum of MA and DAV is taken as the unity of the degree of ionization as in the preceding paper.

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

[10] H. Hotta, ***Mem. Inst. Sci. & Ind. Research Osaka Univ.***, **11**, 179 (1954).

the amine groups perfectly dissociated; from this *p*H, the total degree of ionization is rapidly affected by the appreciable ionization of the acid group; and at *p*H more than about 6 the film becomes soluble, due to the higher degree of ionization of the acid group. Since the effect of the liberation from lateral cohesion due to the oil phase joins the effect of ionization, the dissociation of the acid group is promoted more and more. Therefore, this effect becomes more considerable at the oil/water interface than at the air/water interface if the *p*H of substrate is the same. It should be more considerable in the case of polyelectrolyte having the higher content of the acid group. The difference of *p*H at a bending point between the three figures can be understood in the light of the effect of the oil phase as mentioned above.

From these reasons, the value of $(\pi A)_{A=\infty}$ for sample M up to a bending point (*p*H 3.5) in Fig. 4 might correspond to that in the undissociated state. Therefore, the length of a statistical kinetic unit in atom unit in the main chain at the oil/water interface, n_{atom}, which is derived from $\left(\frac{kT}{\pi A}\right)_{A=\infty}$, for polymethacrylic acid in the undissociated state is 53 (see Table II). In the range of *p*H more than 3.5 the value of $(\pi A)_{A=\infty}$ increases gradually due to ionization. On the other hand, the values for samples K and L are great at the low *p*H range due to the dissociation of the amine group, but decrease sharply when approaching to *p*H 5, and become 17×10^{-16} erg/vinyl unit for both samples at *p*H 5, which seems to be a surface isoelectric point at the air/water interface.[1] Therefore, the value of n_{atom} for them at this *p*H is 47 (see Table II). The value of $(\pi A)_{A=\infty}$ at the high *p*H range is uncertain, due to the high solubility by the dissociation. The detailed meaning for n_{atom} has been already given in the previous papers.[5,10] On comparing the present values in Table II with the previous ones,[10,11] the value of n_{atom} for the previous non-electrolytic linear polymers (polymethyl methacrylate and amilan) is identical to that for samples K and L, and somewhat smaller than that for polymethacrylic acid. The latter fact may be due to the strong cohesion between undissociated acid groups.[1,11] Of course, all the values are compared in the non-electric state.

TABLE II

THE LENGTH OF STATISTICAL KINETIC UNIT IN ATOM UNIT IN THE MAIN CHAIN (n_{atom})

Sample	n_{atom}
K and L at pH 5 (surface isoelectric point)	47
M in undissociated state	53

The values of $(\pi A)_{A=\infty}$ for samples K and L in Fig. 4 are entirely different at least up to *p*H 3.5, while their collapse pressures in Fig. 5 are completely identical in spite of their different composition as shown in Table I. It is concluded from these facts that the amine groups of these copolymers are perfectly dissociated at the larger area at least up to *p*H 3.5 without the mutual restriction of dissociation due to electrostatic interaction. This may be caused by the liberation from lateral cohesion due to the oil phase. However, the difference between them is no more appeared at the narrow area such as a collapse point similar to at the air/water

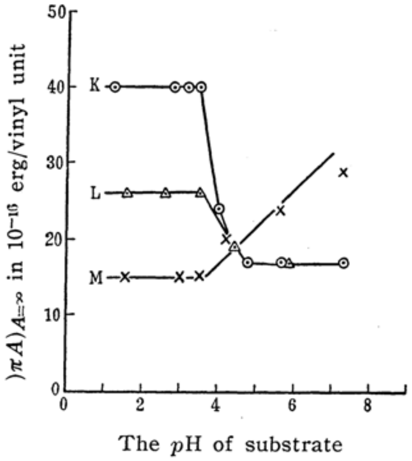

Fig. 4. The $(\pi A)_{A=\infty}$ at the various pH of substrate: ⊙, sample K; ⚠, sample L; and ×, sample M.

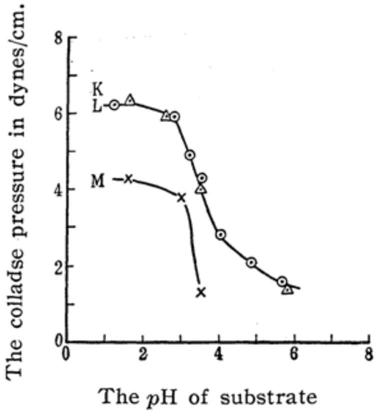

Fig. 5. The collapse pressure at the various pH of substrate: ⊙, sample K; ⚠, sample L; and ×, sample M.

---

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

interface, since their dissociation is considerably restricted due to mutual electrostatic interaction, as in the case of condensed film at the air/water interface, and the side chains are immersed into the aqueous phase as discussed in the preceding paper.1) The present conclusions are also derived from the measurement of interfacial potential as mentioned just below.

The interfacial moments in Figs. 6 and 7 are constant at the area larger than about 50 Å^2 per vinyl unit, and converge at the narrower area so as to become about 100_{m}D at 10 Å^2. When the interfacial moment at the constant range is plotted against the *p*H of substrate in Fig. 8, it has the same tendency as in Figs. 4, 5 and Fig. 7 in the preceding paper,1) which can be interpreted as mentioned above. The points in the negative side of this figure mean only the inversion of sign qualitatively. The interfacial moments for samples K and L up to *p*H 3.5 in Fig. 8 differ considerably from each other, in contrast to their surface moments which are almost identical at the air/water interface. Assuming the perfect dissociation of the amine group and the perfect undissociation of the acid group, the interfacial moment of the dissociated amine group which is evaluated from their interfacial moment at this *p*H range and their composition in Table I, is 600$_{\mathrm{m}}$D for both samples. In this evaluation the interfacial moment of the undissociated acid group is assumed to be 15_{m}D) from the curve of sample M. This value (600$_{\mathrm{m}}$D) is completely identical with to that found at the air/water interface.1) It is analogous to the result reported by Davies6,7) that the surface potential of $C_{18}H_{37}N(CH_3)^+_3$ on 10^{-2} N-NaCl is identical at the air/water and oil/water interfaces. The interfacial moment extrapolated to 10 Å^2 (100 $_{\mathrm{m}}$D) is almost identical with that at 10 Å^2 at the air/water interface.1) These facts correspond exactly to the results of interfacial pressure measurements mentioned above.

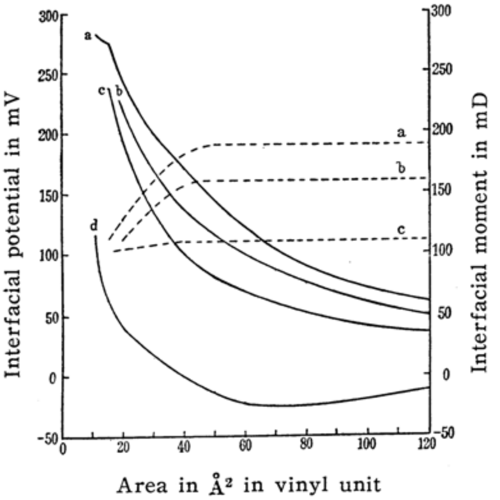

Fig. 6. The interfacial potential (or interfacial moment)-area curves of sample K at the various *p*H of substrate. The interfacial moment-area curve is shown by a dotted line. Curve a, *p*H 1.4 and 3.5; curve b, *p*H 4.2; curve c, *p*H 4.7; and curve d, *p*H 5.6.

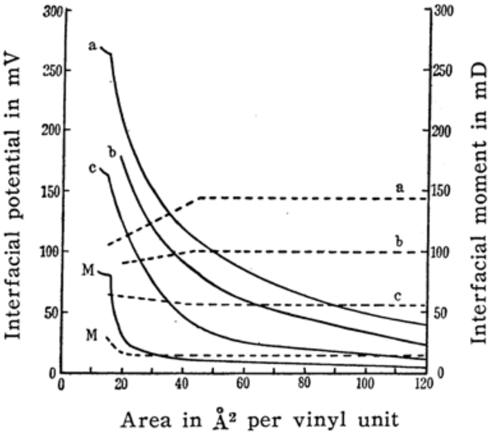

Fig. 7. The interfacial potential (or interfacial moment)-area curves of samples L and M at the various *p*H of substrate. The interfacial moment-area curve is shown by a dotted line. Sample L: curve a, *p*H 1.4 and 3.5; curve b, *p*H 4.2; and curve c, *p*H 4.7. Sample M; curve M, *p*H 1.6.

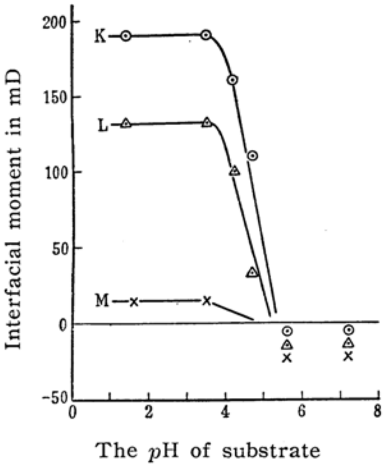

Fig. 8. The interfacial moment at the large area plotted against the *p*H of substrate. ⊙, sample K; △, sample L; and ×, sample M.

The interfacial moment of polymethacrylic acid at the larger area in the undissociated state (15 mD) is far smaller than that in the same state at the air/water interface (90 mD)⁽¹⁾ This difference is due to the difference of the type of film at the two interfaces. With the increase of the content of methacrylic acid and the decrease of the total degree of ionization, the bending point of interfacial moment-area curves shifts to a smaller area and approaches to 30 Å² found at the air-water interface.

Glazer and Dogan[12] recently investigated the state of ionization of insoluble monolayers by the measurement of maximum surface potential at the air/aqueous phase at various *p*H interface. Although they found that the value of *pK* from their surface technique agrees fairly well with that from the measurement in the bulk solution in the case of protein, but not in the case of the low molecules as stearic acid and octadecylamine, they could not explain the latter disagreement satisfactorily. On the other hand, these facts may be understood in the light of our present investigation. The method of maximum surface potential is applicable to protein, which has a rigid structure even at the larger area as well as at a collapse point.[10] But it is unsuitable to low molecules, which have a loosely packed structure between them at the larger area, for the *pK* from bulk solution corresponds to that at an expanded film. To obtain *pK* by the surface technique for such low molecules, the surface moment in a constant range at the larger area should be investigated. Both methods are consistent only in the case, where the surface moment is constant up to a collapse point such as in the case of polymethyl methacrylate and polymethacrylic acid at the undissociated state at the air/water interface.[11] This is the case of protein.

Summary

As the result of the comparison of interfacial pressure and potential of polymethacrylic acid and its copolymers with diethylaminoethyl vinyl ether at the various *p*H of substrate between the air/water and oil/water interfaces, it is concluded that their films are of the expanded type without the mutual restriction of dissociation at the larger area at the oil/water interface, and, on the other hand, they are of condensed type with such a restriction even at the larger area at the air/water interface. The difference at the two interfaces disappears at a collapse point, where these films are of condensed type.

In conclusion, the author expresses his hearty thanks to Professor T. Isemura for his kind guidance throughout the present work, and to Mr. S. Otsuka in the Institute who kindly supplied many samples to him.

The Institute of Scientific and
Industrial Research,
Osaka University,
Sakai, Osaka

---

[12] J, Glazer and M. Z. Dogan, *Trans. Faraday Soc.*, **49**, 448 (1953).