Surface Chemistry of High Polymers. VII[1] *Polyacids and Some Vinyl Polymers*

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As mentioned in the previous paper[2], the study of polyelectrolytes has many interesting points not only for pure physical chemistry but also as an important model of biocolloidal substances. Therefore, some investigations have been carried out along these lines. Especially, the solution of polymethacrylic acid has been studied exhaustively as a typical linear polyelectrolyte[3]. However, the surface film of polyelectrolytes has not been studied thoroughly as yet. In the present experiment, the films of poly-L-glutamic acid and of the copolymer of maleic acid and vinyl acetate were studied at the air/ and oil/water interfaces by measuring their interfacial pressure and potential in order to know the behavior of carboxyl groups as the most important component of polyelectrolytes. The interfacial

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[1] Part VI of this series, H. Hotta, This Bulletin, **28**, 64 (1955).

[2] T. Isemura, H. Hotta and S. Otsuka, ibid., **27**, 93 (1954).

[3] For example, A. Katchalsky, O. Künzel and W. Kuhn, *J. Polymer Sci.*, **5**, 283 (1950); A. Katchalsky, ibid., **7**, 393 (1951).

potential of some non-electrolytic linear polymers and di- and tri-carboxylic acids was also measured for reference in order to elucidate the behavior of the present polyacids. The obtained results were considered in the light of the knowledge of some polyacids, which had been studied previously[2,4,5].

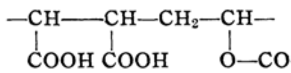
Experimental

The films were spread at the air/and petroleum ether (b. p. 90-130°C)/aqueous phase interfaces, and their interfacial pressure and potential were measured at room temperature. The pH of aqueous phase was adjusted by hydrochloric acid. The apparutus and methods were the same as in the previous papers[2,4]

Materials and spreading solutions used in the present investigation were as follows. The copolymer of maleic acid and vinyl acetate, which was kindly supplied from Sekisui Chem. Ind. Co., Ltd., and polyvinyl alcohol, whose degree of polymerization was 2510, were dissolved in distilled water. Poly-L-glutamic acid, which was the same as that studied previously in our laboratory[6], was dissolved in N/100 sodium hydroxide solution. Isopropyl alcohol was added to all these solutions in the concentration of 20% to help the spreading. Polyvinyl acetate[7], octadecyl malonic acid[6] and hexadecane-1, 1,2-tricarboxylic acid[6] were dissolved in the same solvent as in the previous studies, respectively.

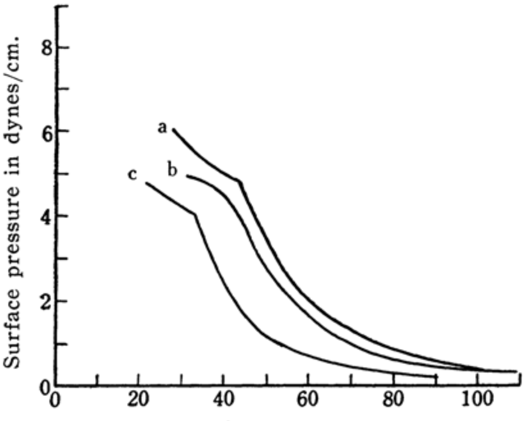
Results

We studied first the film of the copolymer of maleic acid and vinyl acetate on the aqueous phase of various pH. Since this copolymer, which is called hereafter MAVA, has



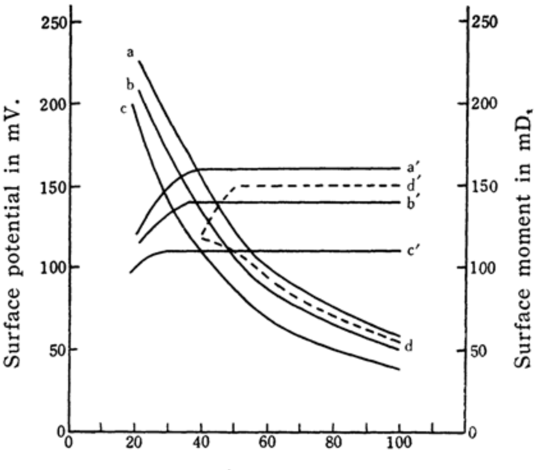
$$-\underset{\text{COOH}}{\text{CH}}-\underset{\text{COOH}}{\text{CH}}-\text{CH}_2-\underset{\text{O}-\text{CO}-\text{CH}_3}{\text{CH}}-$$

as a constitutional unit, figures for this copolymer in the present paper are plotted against the



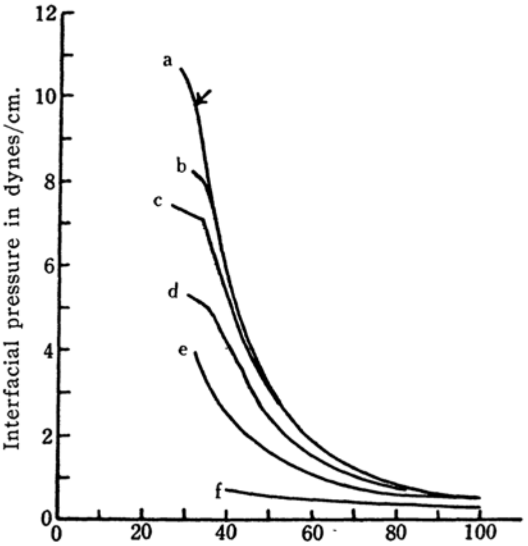
Area in Å²/structural unit

Fig. 1. The surface pressure-area curves of MAVA at the air/water interface (at about 15°C);
curve a (pH 1.6-4.0), curve b (pH 4.4), and curve c (pH 5.2).



Area in Å²/structural unit

Fig. 2. The interfacial potential (moment)-area curves of MAVA at the air/water interface (curve a pH 1.6 and 2.6, curve b pH 3.2 and curve c pH 3.8), and at the petroleum ether/water interface (curve d pH 1.6 containing 2 M KCl) (at about 18°C).



Area in Å²/structural unit

Fig. 3. The interfacial pressure--area curves of MAVA at the petroleum ether/water interface at about 20°C; curve a pH 1.6 and 2.4, curve **b** pH 2.8, curve c pH 3.2, curve d pH 4.0, curve e pH 4.8 and curve f pH 5.6.

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[4] H. Hotta, This Bulletin, **27**, 412 (1954).
[5] H. Hotta and T. Isemura, ibid., **29**, 90 (1956).
[6] T. Isemura and K. Hamaguchi, ibid., **27**, 339(1954).
[7] T. Isemura, H. Hotta and T. Miwa, ibid., **26**, 380 (1953).

area per this unit. The surface pressure and potential at the air/water interface are shown in Figs. 1 and 2, respectively. The corresponding surface moment-area curves in the present paper are represented by prime in the same figure of surface potential. The observed value of surface potential, which will be mentioned later in Fig. 8, was somewhat various, and this tendency was considerable at pH more than 4.0.

The interfacial pressure of MAVA at the petroleum ether/water interface is shown in Fig. 3. The kink point of curve a is shown by an arrow. Curve a of this figure coincides entirely with curve a in Fig. 1 at the moderate area. It means that MAVA gives a film of expanded type like polyvinyl acetate even at the air/water interface[8]. The spreading solution dissolved partially into aqueous phase at the lower pH than at the air/water interface. (See Figs. 1 and 3.) Since the distinct interfacial potential-area curve could not be obtained in the higher pH range at the oil/water interface, only the results on the aqueous phase of pH 1.6 containing 0.2 M potassium chloride is shown with dotted line (curve d) in Fig. 2. In Fig. 2, the surface moments at both interfaces are nearly equal to each other. This is another evidence that MAVA is of expanded state even at the air/water interface, for the film could not have the same configuration, namely, the same surface moment, if it were the film of different type at both interfaces.

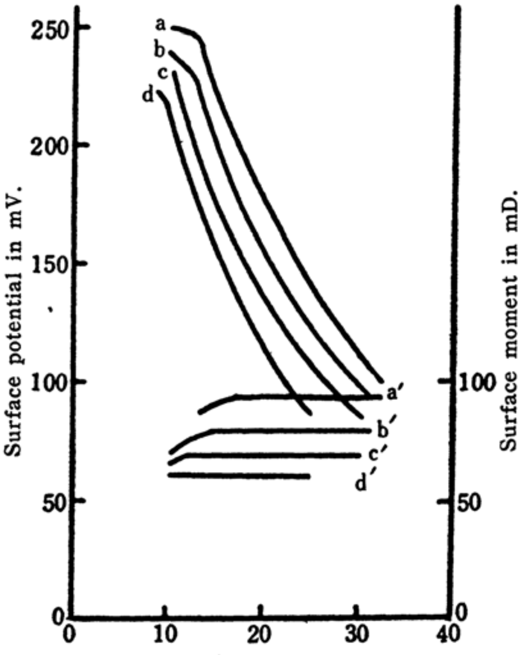

Fig. 4. The surface potential (moment)-area curves of poly-L-glutamic acid at the air/water interface at about 23°C; curve a pH 1.2 and 3.8, curve b pH 4.2, curve c pH 4..8 and curve d pH 5.2.

The surface potential-area curves of poly-L-glutamic acid at the air/water interface are shown in Fig. 4. The surface pressure and viscosity of this polyaminoacid had been reported previously from our laboratory[6]. The reproducible curve could not be obtained at the larger area than $30\,\text{Å}^2$ per residue. Since the interfacial potential-area curve of poly-L-glutamic acid at the oil/water interface could not be obtained due to the partial dissolution of spreading solution into aqueous phase, only the maximum interfacial potential is shown as the function of the pH of aqueous phase in Fig. 5. Nevertheless, the interfacial moment on pH 1.6 might be about 80 mD. The dependence of the maximum interfacial potential on the pH of aqueous phase is similar at both interfaces. (See Figs. 4 and 5.)

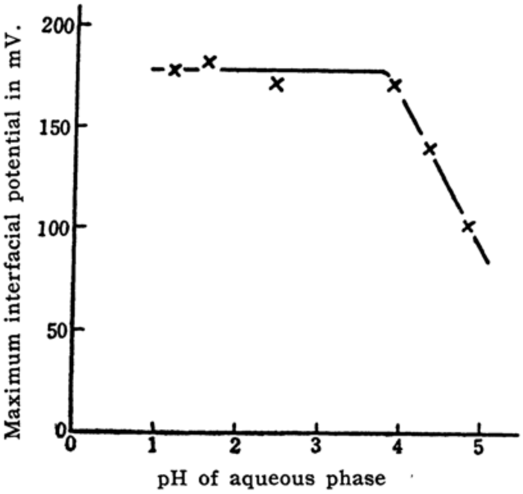

Fig. 5. The maximum interfacial potential of poly-L-glutamic acid at the petroleum ether/water interface on the various pH of aqueous phase.

As the example of simple polyacid, we measured the surface potential of octadecyl malonic acid and hexadecane-1, 1, 2-tricarboxylic acid at the air/water interface (pH 1.6). The surface moments obtained at the larger area are shown in Table I, although the values at the smaller area than $60\,\text{Å}^2$ per molecule show some irregularity. The surface pressure-area relation of these acids had been reported in the preceding paper[5].

On the other hand, we measured the interfacial potential of polyvinyl acetate and polyvinyl alcohol at the petroleum ether/water interface for reference. The result of polyvinyl acetate is shown in Fig. 6, together with the curve at the air/water interface in the previous paper[7]. Since the potential values at the kink point of curves a and b (422 mV.) are quite identical, the true curve at the oil/ water interface may be expected as shown with dotted line, if we take imperfect spreading at the smaller area at this interface into consideration. The interfacial pressure and potential of polyvinyl alcohol at the oil water interface is shown in Fig. 7. The change of interfacial pressure with time appeared at the smaller area than

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[8] H. Hotta, *J. Colloid Sci.*, **9**, 504 (1954).

TABLE I

THE SURFACE MOMENT OF VARIOUS COMPOUNDS

Compound	Formula	Surface Moment in mD		Reference
		at Air/Water Interface	at Oil/Water Interface	
Polyvinyl alcohol	$-CH_2-CH(OH)-$	40	45	12, The present
Polymethacrylic acid	$-CH_2-C(CH_3)(COOH)-$	90	15	2, 4
Poly-4-vinyl benzoic acid	$-CH_2-CH(C_6H_4COOH)-$	100	—	9
Poly-L-glutamic acid	$-NH-\underset{\mid}{CH}-CO$ CH_2CH_2COOH	95	80	The present
Poly-ε-caproamide	$-NH-(CH_2)_5-CO-$	225	—	10
Copolymer of maleic acid and vinyl acetate	$-CH(COOH)-CH(COOH)-CH_2-CH(OCOCH_3)-$	160	150	The present
Octadecyl malonic acid	$CH_3-(CH_2)_{17}-CH(COOH)-COOH$	240	—	The present
Hexadecane-1, 1, 2-tricarboxylic acid	$CH_3-(CH_2)_{16}-CH(COOH)-CH(COOH)-COOH$	200	—	The present
ω-ω′-hexadecane-dicarboxylic acid	$HOOC-(CH_2)_{16}-COOH$	350	—	11
Polyethylene terephthalate	$-O-CO-C_6H_4-CO-O-(CH_2)_2-$	350	—	1
Polyvinyl acetate	$-CH_2CH(OCOCH_3)-$	340a) 280b)	280	7, The present
Polymethyl methacrylate	$-CH_2C(CH_3)(COOCH_3)-$	250	—	10
Polyoctadecyl methacrylate	$-CH_2-C(CH_3)(COOC_{18}H_{37})-$	460	—	12
Myristic acid	$CH_3-(CH_2)_{12}-COOH$	156a) 250b)	—	13

a) An expanded state.
b) A condensed state.

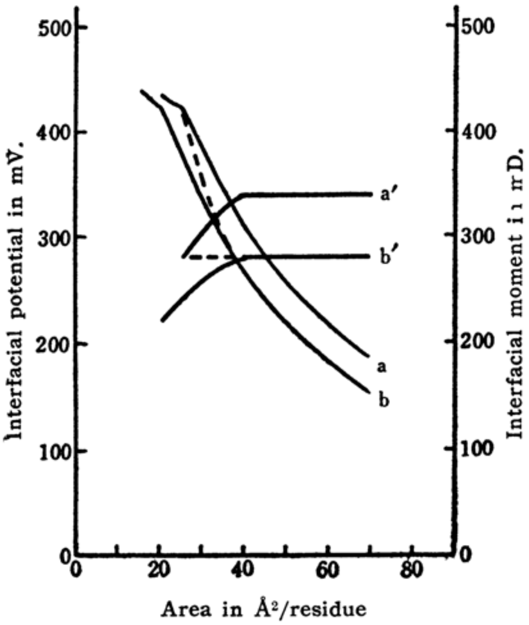

Fig. 6. The interfacial potential (moment)-area curves of polyvinyl acetate at the air/water (curve a) and petroleum ether/water (curve b) interfaces.

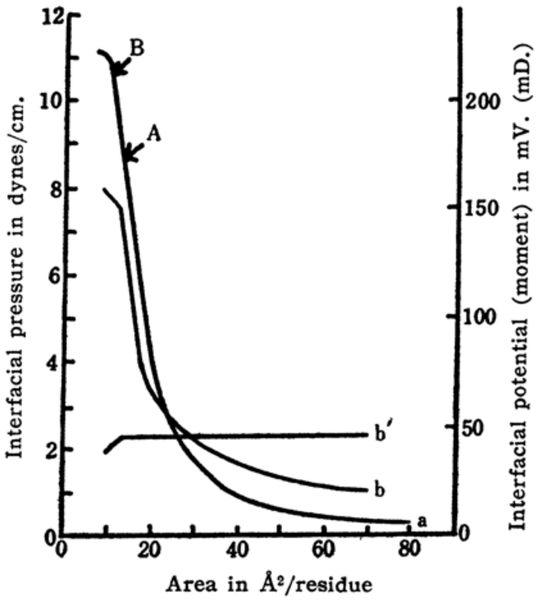

Fig. 7. The interfacial pressure-area curve a and potential (moment)-area curve b of polyvinyl alcohol at the petroleum ether/water interface.

13 Å^2 per monomer (arrow A), where the interfacial moment began to lower. Furthermore, the lowering of the pressure becomes more distinct in the region of the area smaller than 11 Å^2 per monomer (arrow B).

Discussion

As mentioned above, the copolymer of maleic acid and vinyl acetate (MAVA) on pH 1.6 gives a film of expanded type even at the air/water interface. On the other hand, at the air/water interface, polymethacrylic acid gives a film of condensed type on the aqueous phase of pH 1.6 due to cohesion between carboxyl groups(2), and polyvinyl acetate gives a film of expanded type due to the effect of short side chains(7,8) as shown in the previous investigations. It seems that the short side chains in this copolymer still play a role of two dimensional self-plasticizer against cohesion between carboxyl groups.

In the previous paper(8) it was proposed that, when n_{atom} is defined by an equation

$$n_{atom}=a\left(\frac{kT}{\pi A}\right)_{A\to\infty}$$

where a is the number of main atoms in the structural unit of main chain, k Boltzmann's constant, T absolute temperature, π interfacial pressure, A area per structural unit, n_{atom} is a characteristic quantity representing the behavior at the interface. The value of n_{atom} for MAVA was found to be 43, which corresponds to the mean value of 38 for polyvinyl acetate and 48 for methacrylic acid in the previous investigations(8). The value for polyvinyl alcohol was 41.

Since the surface moment of some compounds was measured in the present investigation, we have made a list of them in the non-ionized state or of non-electrolyte with those of other related compounds(9−13) in Table I, in which the value of surface moment is for the represented formula. It may be assumed that the compounds, whose surface moment is nearly equal at both interfaces, have almost the same orientation at both interfaces. For polyvinyl acetate, the moment at the oil/water interface is identical with that at the air/water interface not at the expanded state but at the compact state. It is understood in the light of a previous model(8,10) on account of the affinity of methyl group to oil phase.

The surface moments of carboxyl groups for the polymers examined are quite different as shown in Table I. It might be due to the various orientations of C=O bond as mentioned previously(8,10). Generally speaking, it appears that the horizontal orientation of a chain directly linking to the carbon atom of carboxyl group makes the surface moment lower, and that this tendency of lowering is more predominant for the closer approach of carboxyl groups with each other (for example, hexadecane-1, 1, 2-tricarboxylic acid). The surface moment of MAVA and of poly-L-glutamic acid can not be explained by the additivity of the constituent polar groups cited in Table I. (Polymethacrylic acid and polyvinyl acetate for MAVA, or polymethacrylic acid and poly-ε-caproamide for poly-L-glutamic acid) It might be attributed to the change of mutual orientation of these polar groups at the interface.

Besides, we must consider the ionization effect of carboxyl groups for polyacids with increasing pH of aqueous phase. Especially, the surface moment is most sensitive to this effect, and is lowered due to the ionization of the acid group. When the surface moment of polyacids in the range of constant value at the air/water interface are plotted against the pH of aqueous

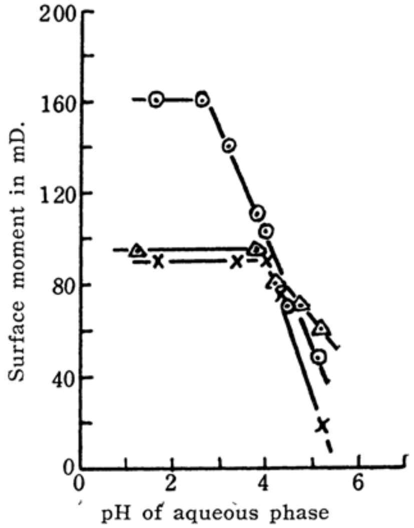

Fig. 8. The surface moment of polyacids at the constant range at the air/water interface plotted against the pH of aqueous phase; MAVA (◉), poly-L-glutamic acid (△) and polymethacrylic acid (×).

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

10) H. Hotta, This Bulletin, **27**, 80 (1954)

11) H. Hotta and T. Isemura, ibid., **25**, 101 (1952).

12) D. J. Crisp, *J. Colloid Sci.*, **1**, 161 (1946).

13) J. H. Schulman and E. K. Rideal, *Proc. Roy. Soc.* (London), **130A**, 270 (1931).

phase in Fig. 8, we find that the bending points of these curves correspond almost to the pK of the monomer unit of these polyacids, which is 2.85, 4.25 and 4.85 for malonic acid, glutamic acid and isobutyric acid in this case, respectively. The values of surface moment of MAVA at pH more than 4.0 in Fig. 8 are the mean values of the repeated experiments, for they were various as mentioned above. The curve for polymethacrylic acid is cited from the previous results[3].

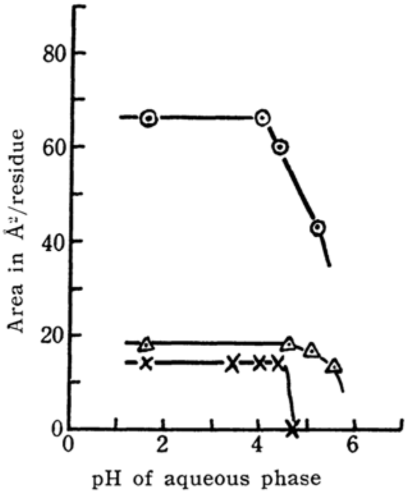

Fig. 9. The area of polyacids at the constant surface pressure (1 dyne/cm.) at the air/water interface plotted against the pH of aqueous phase (at 10-15°C); MAVA (⊙), poly-L-glutamic acid (△) and polymethacrylic acid (×).

On the other hand, the similar relationship was not found for surface pressure as shown in Fig. 9, in which the curves for poly-L-glutamic acid[6] and polymethacrylic acid[2] are cited from the previous results. In the case of surface pressure, the contribution of the non-ionizable part might be fairly effective even in the region of larger pH. Although the lowering of these curves with increasing pH is due to the partial dissolution, this would be determined not only by the degree of ionization but also the hydrophylic nature of non-ionizable part and the state of the molecule. It is necessary for complete ionization that the electrostatic repulsion between ionic groups must overcome the intramolecular cohesion (van der Waals' force or hydrogen bonding)[2,8]. All pH's at the point, where the lowering occurs, are between 4 and 5.

It is more or less difficult to obtain the distinct result not only in the ionized state, but also in the non-ionized state for polyacids studied in the present investigation except for polymethacrylic acid which gives a film of condensed type. The surface pressure changes more or less with time. The similar result is reported for polybenzoic acid[9]. It may be caused by the gelation due to hydrated carboxyl groups.

Summary

The films of polyacids (poly-L-glutamic acid and the copolymer of maleic acid and vinyl acetate) and some related compounds were studied in order to know the behaviour of carboxyl groups in the linear polymer at the interface. The principal results obtained are as follows.

The orientation of carboxyl group is affected considerably by other accompanying groups in polymer. Hence, the surface moment of carboxylic compounds is various according to the surface orientation of respective groups in the polymer. Accordingly, the surface moment of copolymer cannot be explained by the simple additivity of the moment of constituent polar groups.

The surface moment of polyacids abruptly decreases nearly at the pH of aqueous phase equal to the pK of corresponding structural unit.

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