Viscosity and osmotic second virial coefficient of maleic acid copolymers in aqueous solutions

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Unperturbed dimensions or characteristic ratios of maleic acid copolymers (MA-copolymers) in aqueous solutions were estimated for various degrees of neutralization, α, to clarify the abnormal α-dependence of viscosity of MA-copolymers in more detail. The dependence of the osmotic second virial coefficient A_2 on α was measured in NaCl aqueous solution. A_2 was analysed by the Fixman–Skolnick theory on account of the activity coefficients of counterions at various α's. The characteristic ratio seems nearly constant, $\sim$10, independent of α, and the maximum at $\alpha = 0.5$ is not observed. A_2 increases with increase of α up to $\alpha = 0.5$ and decreases with further increase in a corresponding to the α-dependence of viscosity. Fairly good agreement between the experimental and theoretical values of A_2 is observed. Theoretical values of A_2, however, increase monotonically with increase in α. Our experimental results show that the α-dependences of viscosity and A_2 of MA-copolymers in aqueous solutions should be attributed to a change of hydration structure of the pair of adjacent carboxyl groups with neutralization.

INTRODUCTION

Alternating copolymers of maleic acid(MA-copolymers) possess many characteristic properties in aqueous solutions[1-4]. One of their most remarkable behaviours is the change in the viscosity with neutralization. The viscosity exhibits a maximum at the half-neutralization point and decreases largely with further increase in degree of neutralization, α, when solutions are neutralized with bases[5,6,1]. Usually, viscosities of most weak polyelectrolyte solutions increase with increase of α. The viscometric behaviour of the maleic acid copolymers seems an abnormal phenomenon from the viewpoint that the expansion of polyelectrolytes in aqueous solution originates mainly in the repulsive electrostatic interaction among charges on polyions.

A few interpretations on the α-dependence of the viscosity of MA-copolymers have been reported[7-9]. The experimental facts, however, could not be explained satisfactorily by these interpretations. For example, an excess binding of counterions at $\alpha > 0.5$ has been proposed because of the existence of maximum at $\alpha = 0.5$ with poor experimental evidence.[9]

It is thought necessary to investigate the local conformations of the polymer chain in aqueous solution and the interactions between solvent (water molecules) and the polyion at various α values to clarify the α-dependence of viscosity of MA-copolymers more accurately. In this article, we have tried to understand the viscometric properties of MA-copolymers in aqueous solution in a relation between unperturbed dimensions at various α values and α-dependence of the osmotic second virial coefficient A_2. In addition, A_2 was analysed theoretically on the basis of the measured activity coefficients of counterions at various α's.

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EXPERIMENTAL

Polymerization of the alternating copolymer of maleic anhydride and ethyl vinyl ether (MAEVE) was carried out in benzene with 2,2'-azobisisobutyronitrile as initiator at 60°C for 5 h. The details of polymerization, purification and characterization have been described elsewhere[10,11]. The weight-average molecular weight $\bar{M}_w$ were 4.5×10^4, 2.8×10^5, and 6.6×10^5, respectively. The alternating copolymer of maleic anhydride and ethylene (MAE) ($\bar{M}_w = 2.10^4$) was kindly gifted by the Mitsubishi-Monsanto Chem. Co.

Hydrolysis of MAEVE and MAE was performed by stirring the copolymers in 0.5N NaOH for half a day at room temperature. The solutions were dialysed against deionized distilled water for three days and deionized with an ion exchange column in the H^+-form. The details of the preparation of solutions were reported elsewhere[10,12].

Solution viscosities were measured at 25°C using an Ubbelohde-type viscometer of flow time 167.5 s for pure water. Osmotic pressure measurements were made with a Knauer High-Speed Membrane Osmometer at 30°C. The membranes were regenerated cellulose membranes (Sartorius SM11536). A Na^+-sensitive solid membrane electrode (Orion Research Inc.) was used in combination with a KCl saturated reference electrode (Orion, model 20-02). Potentials were measured using an Orion 701 digital electrometer. The experimental procedures were identical to those previously described in detail[10,12].

RESULTS

In *Figure 1*, reduced viscosities, η_{sp}/C_p, vs. degree of neutralization α, are plotted for MAEVE and MAE in salt-free solutions neutralized with NaOH. The reduced

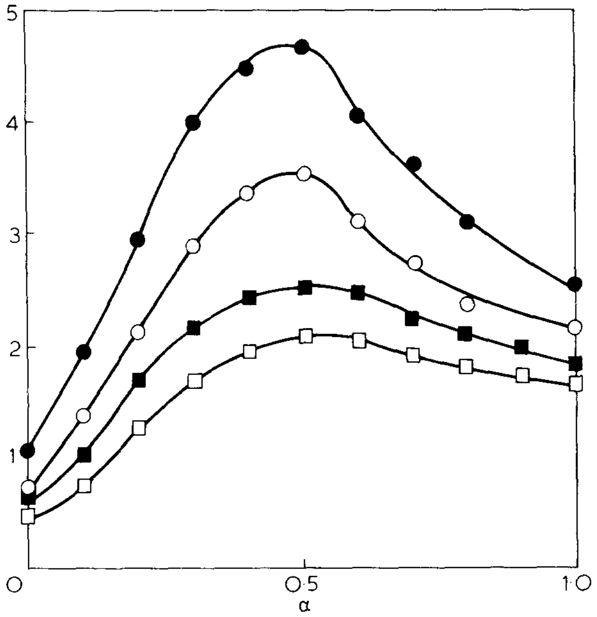

Figure 1 Reduced viscosoties η_{sp}/C_p vs degree of neutralization α of MAEVE ($\bar{M}_w$ = 2.8 x 10^5) (○, ●) and MAE (□, ■) neutralized with NaOH at 25°C. (○), C_p = 2.4 mN; (●), C_p = 1.2 mN; (□), C_p = 4.3 mN; (■), C_p = 2.2 mN. Ordinate is an arbitrary scale

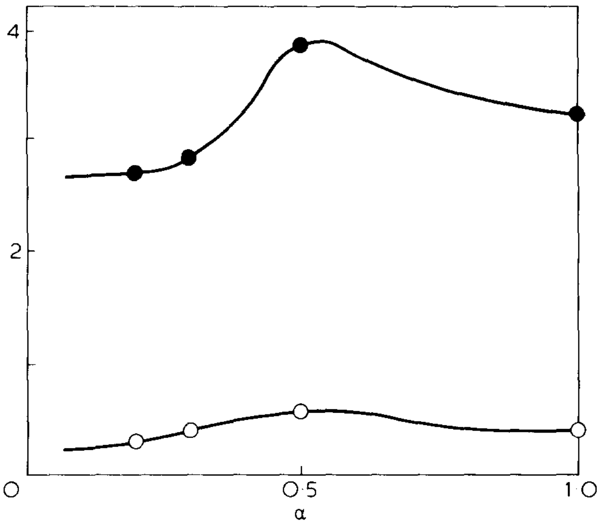

Figure 2 Intrinsic viscosities [η] (dl/g) vs degree of neutralization α of MAEVE in 0.18 M NaCl aqueous solution neutralized with NaOH at 25°C. (○), $\bar{M}_w$ = 4.5 x 10^4; (●), $\bar{M}_w$ = 6.6 x 10^5

viscosity increases largely up to $\alpha=0.5$ and decreases with further increase of α: η_{sp}/C_p exhibits a maximum at $\alpha=0.5$ for both the copolymers. The identical behaviours (maxima at $\alpha=0.5$) of intrinsic viscosities [η] have been observed in simple salt solutions as shown in *Figure 2*. These properties of viscosity, moreover, have been recognized irrespective of the size of hydrophobic side chains (e.g., isobutyl copolymer[1] or poly maleic acid[6]), and hence the hydrophobic effect is not thought to be responsible for the viscometric behaviour vs. α of MA-copolymers.

Next, we estimated the unperturbed dimensions, K_0, or the characteristic ratio, C_∞, of MAEVE for several α values from the measured intrinsic viscosities by the Stockmayer–Fixmann procedure according to the equation[13]

$$[\eta]/M^{1/2}=K_0+0.51\Phi BM^{1/2} \tag{1}$$

In equation (1), Φ is the Flory constant and its value is assumed to be[14] $\Phi=2.6\times10^{21}$ (for [η] in dl/g), *B* is a constant related to the second virial coefficient.

The value K_0 is related to the characteristic ratio C_∞ by

$$C_\infty=(K_0/\Phi)^{2/3}M_0/2l_0^2 \tag{2}$$

where M_0 is a half value of the monomer molecular weight (i.e., 116 for $\alpha=1.0$ and 94 for $\alpha=0.0$) and l_0 is the bond length (i.e., 1.54 Å for a C–C bond[15]).

The plots of $[\eta]/\bar{M}_w^{1/2}$ vs. $\bar{M}_w^{1/2}$ are shown in *Figure 3* according to equation 1 for MAEVE in aqueous NaCl solutions neutralized with NaOH at several α values. The intercepts obtained from equation 2, and the corresponding values of C_∞ calculated from equation 2 by using the value of M_0 for each α are listed in *Table 1*.

Contrary to the behaviour of the intrinsic viscosity vs. α, the C_∞ value seems nearly constant, i.e., ~10, independent of α, and the maximum at $\alpha=0.5$ is not detected, though the data values are scattered.

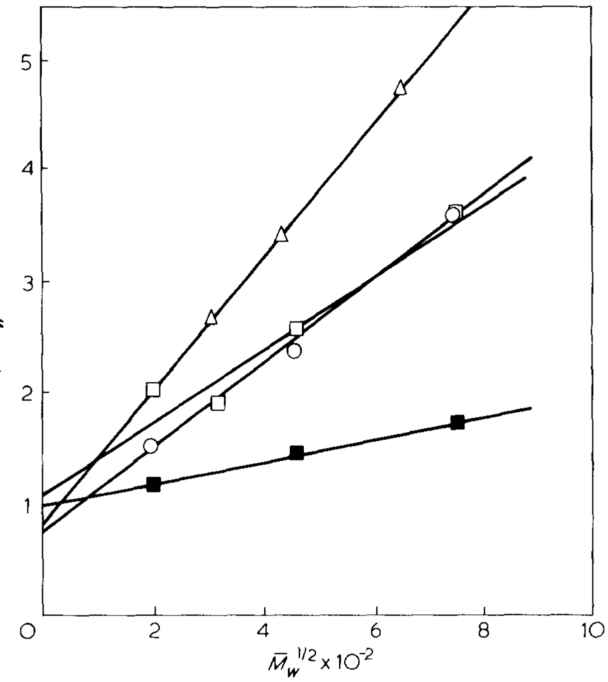

Figure 3 Stockmayer–Fixman plots of MAEVE in NaCl aqueous solutions for various α values at 25°C. (○), α = 0.2, 0.18M NaCl; (□), α = 0.3, 0.18M NaCl; (■), α = 0.3, 2.00M NaCl, (△), α = 0.5, 0.18M NaCl

Table 1 Unperturbed dimension K_0 and characteristic ratio C_∞ of MAEVE in aqueous NaCl solutions at various α values at 25°C

α	C_s (M)	K_0	M_0	C_∞
0.0*	–	8.7	94	9.6*
0.2	0.18	7.0	98.4	8.7
0.3	0.18	11.3	100.6	12.2
	2.00	9.9		11.2
0.5	0.18	7.9	105	10.0
1.0**	0.18	7.6	116	10.8**

* Estimated in organic solvents (ref 11)
** From ref 11

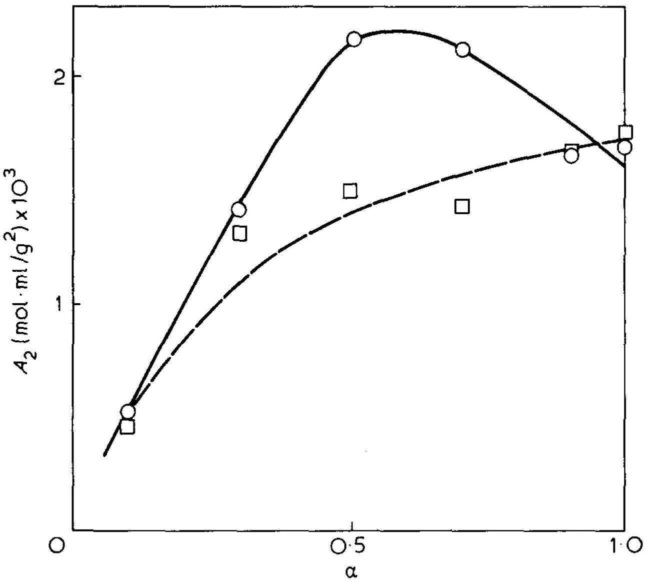

Figure 4 Second virial coefficient vs α of MAEVE in 0.18M NaCl aqueous solution at 25°C. (○), experimental data; (□), theoretical values estimated from the Fixman–Skolnick theory on account of the activity coefficient of counterions

Furthermore, the maximum of intrinsic viscosity at $\alpha = 0.5$ tends to diminish with increasing the concentration of simple salts C_s.[16] This means that the expansion of this copolymer chain is almost independent of the degree of neutralization at theta condition. That is, the unperturbed dimensions do not reflect the local conformation of the polymer chain which may be determined from the degree of neutralization of the pairs of carboxyl groups on the polyion. It is a reasonable result, since the short-range electrostatic interaction also disappears effectively due to the shielding effect of the counterion atmosphere at the theta condition.

Osmotic second virial coefficients A_2 (mol·ml/g^2) vs. α are plotted in *Figure 4* for MAEVE in 0.18M NaCl aqueous solutions neutralized with NaOH. A broken line and square symbols in the same figure are the theoretical values estimated from the Fixman–Skolnick theory on the basis of activity coefficients γ_+'s of sodium ions discussed in detail in the Discussion section. A_2 increases with increase in α up to $\alpha = 0.5$ and decreases with further increase in α, that is, A_2 exhibits a maximum around the half-neutralization point corresponding to the α-dependence of viscosity.

It may be concluded, from our experimental results, that the viscometric behaviour of MA-copolymers against the degree of neutralization, α, in aqueous solutions do not relate directly to the unperturbed dimensions of the copolymer chain but to the mechanism which is responsible for α-dependence of A_2.

DISCUSSION

In *Table 2*, the experimental osmotic second virial coefficients A_2 of MAEVE in aqueous NaCl solutions are listed for various NaCl concentrations, C_s, and compared with the theoretical values. Clearly, A_2 is linearly dependent on $C_s^{-1/2}$. The theoretical values of A_2 have been calculated in the following manner.

According to the Fixmann–Skolnick theory,[17] the osmotic second virial coefficient is given by the relationship

$$A_2 = N_{AV} R(w) h(\bar{z}) / \kappa m_1^2 \tag{3}$$

with

$$R(w) = \int_0^{\pi/2} d\theta \sin\theta [Ei(w/\sin\theta) + \ln(w/\sin\theta) + \gamma] \tag{4}$$

where Ei is the exponential integral and γ is Euler's constant. Other parameters in equations 3 and 4 are represented as follows,

$$w \cong 136.4 I^2 / l^2 C_s^{1/2}, \tag{5}$$

$$\kappa^{-1} \cong 3.043\text{Å}/C_s^{1/2}, \tag{6}$$

and

$$m_1 = m_0/l, \tag{6}$$

where m_0 and l are the molecular weight of a monomer unit and the monomer unit length in Å, respectively, and C_s is expressed in mol l^{-1}. In equation 3, N_{AV} is Avogadro's number and $h(\bar{z})$ is the dimensionless intermolecular excluded volume function[18]. For our present purposes, we have simply assumed $h(\bar{z}) = 0.5$ according to the Fixmann–Skolnick treatment[17,18]. In equation 5, I is the mean number of elementary charges on a monomer unit, i.e., I is the degree of ionization. In comparison with the experimental data with equation 3, values of $m_0 = 116$ g/mol and $l = 2.6$ Å have been used. The value $l = 2.6$ Å is inferred from the titration and thermodynamic studies[12,19]. We have assumed that $I = \alpha \cdot \gamma_+$ with α the degree of neutralization and γ_+ the activity coefficient of the counterions, and have employed a value $\gamma_+ = 0.283$, which was measured by an ion-selective method in salt-free solutions, i.e., $I = 0.283$ at $\alpha = 1.0$.

The agreement between theory and experiment seems good enough to judge the Fixman–Skolnick theory as sufficiently appropriate for our systems. Next, we have estimated the theoretical values of A_2 for various α's using the same values of the parameters on account of the activity coefficients of the counterions (i.e., Na$^+$ ions) and compared them with the experimental data. The results are summarized in *Table 3* and plotted in *Figure 4*.

The theoretical values are in fair agreement with the experimental values semiquantitatively. Nevertheless, the theoretical A_2 increases monotonically with increase in α and exhibits no maximum in contrast to the experimental data. If extremely small values of γ_+ are presumed at $\alpha > 0.5$, the decrease in A_2 with α, i.e., the existence of maximum of A_2 at $\alpha = 0.5$, could be interpreted successfully by the theory.

Table 2 Experimental osmotic second virial coefficients compared with the Fixman–Skolnick theory at various concentrations of NaCl at 25°C

C_s (M)	I	$A_2 \times 10^3$ (experimental)	$A_2 \times 10^3$ (theory)
1.85	0.283	0.78	0.74
0.915	0.283	0.43	0.45
0.180	0.283	1.86	1.66
0.050	0.283	5.48	4.11
0.020	0.283	8.35	7.57
0.010	0.283	12.4	11.8
0.005	0.283	19.0	18.4

Table 3 Dependence of second virial coefficient A_2 on degree of neutralization α. Comparison between the experimental osmotic second virial coefficients and the theoretical values estimated from the Fixman–Skolnick theory

α	$\gamma_\pm$*	I	m_1	l (Å)	$A_2 \times 10^3$† (experimental) (mol. ml/g^2)	$A_2 \times 10^3$† (theory) (mol. ml/g^2)
0.1	0.80	0.080	37.0	2.6	0.54	0.43
0.3	0.552	0.166	38.7	2.6	1.43	1.29
0.5	0.409	0.205	40.4	2.6	2.19	1.52
0.7	0.297	0.208	42.1	2.6	2.13	1.43
0.9	0.283	0.255	43.8	2.6	1.64	1.68
1.0	0.283	0.283	44.6	2.6	1.70	1.80

* Determined in salt-free solutions for C_p = 7.16 mN at 25°C

Our thermodynamic experiments have demonstrated that the interaction between carboxyl polyions and counterions such as Na^+ ions and Ca^{2+} ions is purely electrostatic, and consequently the assumption is proved to be unlikely. Therefore, the fact that A_2 decreases with α for $\alpha > 0.5$ is not thought to be attributable to excess binding[9] of counterions to the polyion.

It is known that the solubility of MA-copolymers displays a maximum at $\alpha = 0.5$ in aqueous solutions and decreases suddenly with increasing α for $\alpha > 0.5$[4]. The solubility should be attributable primarily to the hydration of the pair of adjacent carboxyl groups. The transision-like α-dependence of the solubility means that the hydration structure is different between the regions $0 \leqslant \alpha \leqslant 0.5$ and $0.5 < \alpha \leqslant 1.0$. This originated probably in a local conformational change in the pair of adjacent carboxyl groups around $\alpha = 0.5$ due to the short-range electrostatic interaction between the pair.

It can be concluded that the α-dependence of A_2 of MA-copolymers should be ascribed to the change in affinity of the pair of adjacent carboxyl groups to water molecules with neutralization. Also the dependence of viscosity on α should be explained in terms of the affinity of the pair of adjacent carboxyl groups to water molecules that is caused fundamentally by the short-range electrostatic interaction.

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REFERENCES

1 Dubin, P. and Strauss, U. P. *J. Phys. Chem.* 1967, **71**, 2757
2 Begala, A. J. and Strauss, U. P. *J. Phys. Chem.* 1972, **76**, 254
3 Fenyo, J. C., Delben, F., Paoletti, S. and Crescenzi, V. *J. Phys. Chem.* 1977, **81**, 1900
4 Shimizu, T. in: '1st A. Katchalsky Meeting, Dynamic Processes in Polyion Systems and Electrokinetic Aspects of Biomembranes' (Ed. F. Oosawa *et al.*) Kodansha-Elsevier, Tokyo and Amsterdam, 1980, in press
5 Dubin, P. L. and Strauss, U. P. *J. Phys. Chem.* 1970, **74**, 2842
6 Lang, J. L., Pavelich, W. A. and Clarey, H. D. *J. Polym. Sci. (A)* 1963, **1**, 1123
7 Dubin, P. and Strauss, U. P. *J. Phys. Chem.* 1973, **77**, 1427
8 Barone, G., Di Virgilio, N., Elia, V. and Rizzo, E. *J. Polym. Sci. Symposium No. 44*, 1944, 1
9 Shultz, A. W. and Strauss, U. P. *J. Phys. Chem.* 1972, **76**, 1767; Miyamoto, S. *Ph.D. Thesis*, Nagoya University, 1980
10 Shimizu, T., Minakata, A. and Tomiyama, T. *Polymer* 1980, **21**, 1427
11 Shimizu, T. *Polymer* 1981, **22**, 231
12 Shimizu, T., Minakata, A. and Imai, N. *Biophys. Chem.*, to be published
13 Stockmayer, W. H. and Fixman, M. *J. Polym. Sci. C*, 1963, **1**, 137
14 Flory, P. J. 'Statistical Mechanics of Chain Molecules', Interscience, New York (1969)
15 Morawetz, H. 'Macromolecules in Solutions', 2nd edn, Wiley-Interscience, New York (1975)
16 Shimizu, T., unpublished data
17 Fixman, M. and Skolnick, J. *Macromolecules* 1978, **11**, 863
18 Nagasawa, M. and Takahashi, A. in 'Light-Scattering from Polymer Solutions', (Ed. M. B. Huglin), Academic Press, New York (1972), Chapter 16
19 Sasaki, S. and Minakata, A. *Biophys. Chem.* 1980, **11**, 199