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THE RELEASE OF MONOVALENT COUNTERIONS BY ADDITION OF DIVALENT COUNTERIONS TO AQUEOUS SOLUTIONS OF MALEIC ACID COPOLYMER

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Divalent cation binding and the release of monovalent cations accompanying the cation binding were experimentally studied by ion-selective electrode methods in aqueous solutions of copolymer of maleic acid and ethyl vinyl ether. It was found that in the process of Ca^{2+} addition, all the Ca^{2+} added was bound to polyions and the initially condensed Na^+ was released in proportion to the concentration of the added Ca^{2+} up to the critical concentration of added Ca^{2+} at which the condensation of Ca^{2+} ceases. Values of the structural charge density parameter ξ_s were determined from the end-points of condensation of Ca^{2+}. The process of Na^+ release by adding Ca^{2+} was analyzed on the basis of the counterion condensation theory by using these ξ_s values. In addition, the relationship between the activity coefficient γ_{++} of Ca^{2+} and degree of neutralization α in salt-free solutions was obtained from the Manning theory. Agreement between the calculated and experimental values was excellent in both cases.

1. Introduction

Polyelectrolytes, having a dense distribution of ionizable groups, produce a strong electrostatic field which tightly attracts the dissociated counterions.

When the charge density exceeds a certain critical value, the excess part of counterions is trapped around the polyion. This phenomenon is the well known 'counterion condensation' [1–3]. In a mixture of two kinds of counterions having different valencies, such as monovalent and divalent counterions, polyvalent counterions are preferentially condensed on the polyion at first, and if the charge density is still sufficiently high, the monovalent counterions are condensed next. There have been many experimental investigations examining this competitive binding phenomenon [4–7]. Many experiments have confirmed the above behavior expected by the counterion condensation theory for mixture systems [8–14].

The following behavior is also deduced from the counterion condensation theory. When polyvalent counterions are added to a system including only monovalent counterions, the initially condensed monovalent counterions must be liberated by the preferential binding of the polyvalent counterions. There has been no experimental study as yet, however, on such an interesting problem. It seems important to investigate, for example, what amount of initially condensed monovalent counterions is released and to what degree added polyvalent counterions are bound to polyions in the process of adding polyvalent counterions for a further comprehension of the competitive counterion binding.

An activity measurement of monovalent and divalent counterions in polyelectrolyte solutions

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by electrochemical techniques is one of the most straightforward procedures to confirm the above problem experimentally. In our present work, we measured the changes in activities of Na^+ and Ca^{2+} in solutions of the sodium salt of a copolymer of maleic acid and ethyl vinyl ether (MAEVE) in the process of adding Ca^{2+} (as $CaCl_2$).

The interaction between Ca^{2+} and polycarboxylate had been considered to be specific rather than purely electrostatic [10,15]. Our recent experimental study has indicated that the additivity rule for Ca^{2+} activity is completely established in the process of Ca^{2+} addition to the calcium salt of MAEVE in the absence of other cations [16]. This means that the interaction between Ca^{2+} and this copolymer is mainly electrostatic, since the establishment of the additivity rule is one of the indications of pure electrostatic binding. Therefore, the experimental results in this system can be interpreted in the counterion condensation theory which is based on the electrostatic interaction between counterions and polyions.

Maleic acid copolymer (MA-copolymer) consists of an alternate sequence of a pair of carboxyl groups and a hydrophobic side chain. Several characteristic types of behavior resulting from the interaction between the nearest-neighbour carboxyl groups have been observed in solutions of MA-copolymers [17–23]. For example, pH titration curves for the MA-copolymers neutralized by base exhibit a sharp equivalent point at a half-neutralization point [17–22]. Also, the critical concentration of divalent cations needed to precipitate the polymer shows a transition-like behavior around the half-neutralization point [23].

One of the most important reasons why MAEVE was chosen is that MAEVE never precipitates easily in aqueous solutions with divalent cations under any condition because of the high affinity of the oxygen atom in the ether part for water.

2. Experimental

Polymerization of an alternating copolymer of maleic anhydride and ethyl vinyl ether was carried out in benzene with 2,2′-azobisisobutyronitrile as initiator at 60°C for 5 h. The details of the procedure of polymerization and purification have been described elsewhere [24,25]. The weight-averaged molecular weight was 2.8×10^5. Stock solutions of the polyacid were prepared as described previously [23]. The concentration C_p of the polyelectrolytes was determined by potentiometric titration with $Ba(OH)_2$ in the presence of 2 N NaCl. A solution of the desired degree of neutralization was obtained by adding calculated amounts of NaOH solution to the stocked solution of the polyacid in a volumetric flask.

Deionized distilled water was used in all solutions. Guaranteed grades of $CaCl_2$, $Ca(OH)_2$ and NaOH (Katayama Chem. Co., Nagoya) were used without further purification.

An Na^+-selective solid membrane electrode and a Ca^{2+}-selective liquid membrane electrode (Orion Research Inc., Cambridge, MA) were used with a combination of a KCl-saturated reference electrode (Orion, model 90-02) and an Ag/AgCl reference electrode (Orion, model 90-01). Potentials were measured by a 701 digital electrometer (Orion Research Inc.). The potential readings were carried out with an accuracy within 0.02 mV under the optimum condition for both Ca^{2+}-activity and Na^+-activity measurements.

The electrodes were calibrated with $CaCl_2$ and NaCl solutions of known concentrations. The cation activities in these salt solutions were obtained from the literature values [26]. The observed Nernst slopes of the calibration curves were larger than 22 mV/decade for Ca^{2+} and 56 mV/decade for Na^+ (cf., theoretical values are 29.6 mV/decade for Ca^{2+} activity and 59.1 mV/decade for Na^+ activity). A Hitachi-Horiba pH-meter and a hydrogen-ion glass electrode were used for the pH measurements.

All measurements were performed at 25°C under nitrogen gas to prevent access of CO_2 from the air. Prior to each measurement, the entire system was allowed to equilibrate for at least 1 h. The solutions were stirred continuously during the measurements.

The pH electrode and the Ca^{2+}-selective electrode (or the Na^+-selective electrode) were inserted into an MAEVE solution whose α is 0.5 or 1.0 at a fixed C_p to obtain pH and Ca^{2+} (or Na^+)-activity simultaneously. A 0.5 ml microburette (Metrohm Herisau E457, finest scale division of 0.1 μl) was used to control the addition of $CaCl_2$ to the solutions. The potential reading reached its equilibrium value in 5 min after each addition of a small amount of $CaCl_2$ to the solution. The pH influence on the Ca^{2+}- and Na^+-selective electrodes could be neglected in all cases, i.e., in all solutions, pH values were larger than the critical pH, over which activity measurements of Na^+ and Ca^{2+} could be made safely without H^+ interference (e.g., about pH 5 for 10^{-3} M Na^+).

All measurements were repeated at least twice. Reproducibility was satisfactory (within 3%). The interference on the Na^+ electrode by Ca^{2+} or that on the Ca^{2+} electrode by Na^+ was not at all serious under the conditions of our experiments.

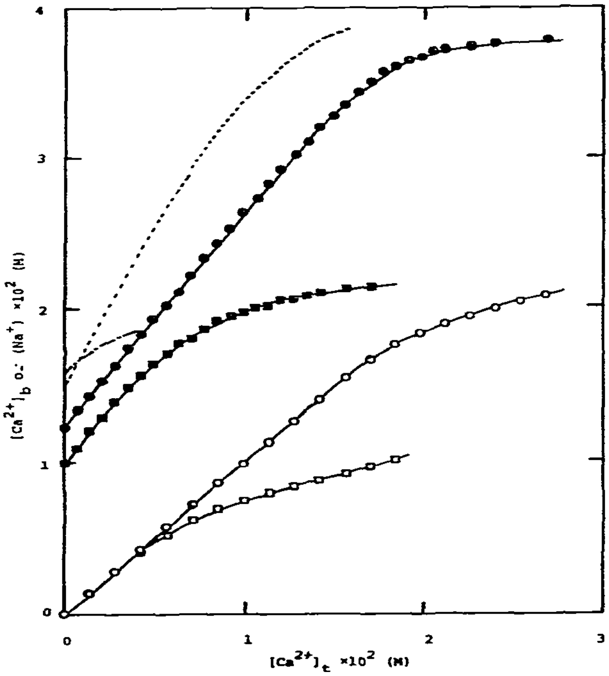

Fig. 1. Variations of the activities of Na^+, (Na^+) (●, ■), and the concentrations of bound Ca^{2+}, $[Ca^{2+}]_b(=[Ca^{2+}]_t-(Ca^{2+}))$ (○, □), with the total concentration of added $CaCl_2$, $[Ca^{2+}]_t$, at $C_p=4.30\times10^{-2}$ N. (□, ■) Degree of neutralization $\alpha=0.5$, (○, ●) $\alpha=1.0$. (— — —, —·—·—) Theoretical values (see text).

3. Results

In fig. 1, the activity of Na^+, (Na^+), and the concentration of bound Ca^{2+}, $[Ca^{2+}]_b(=[Ca^{2+}]_t-(Ca^{2+}))$, were plotted against the concentration of added $CaCl_2$ in the solution of the sodium salt of MAEVE at a fixed polyion concentration ($C_p = 4.30\times10^{-2}$ N) for two values of the degree of neutralization ($\alpha = 0.5$ and 1.0). As seen in fig. 1, the concentration of bound Ca^{2+}, $[Ca^{2+}]_b$, increases in proportion to the stoichiometric concentration of added $CaCl_2$, $[Ca^{2+}]_t$, up to a certain value of $[Ca^{2+}]_t$ in each case. Proportionality constants are exactly unity. This implies that all of the added Ca^{2+} is bound completely to the polyion in this region. Above those critical values of $[Ca^{2+}]_t$, $[Ca^{2+}]_b$ commences to deviate from the straight line and reaches a constant value gradually, showing saturation of the Ca^{2+} binding. In this process, Na^+ activity, (Na^+), increases linearly with increase in $[Ca^{2+}]_t$ up to the critical concentration which coincides with the critical

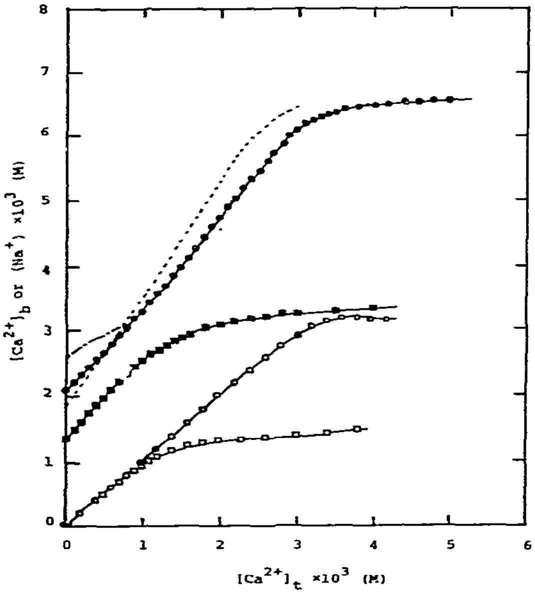

Fig. 2. Variations of (Na^+) (●, ■) and $[Ca^{2+}]_b$ (○, □) with $[Ca^{2+}]_t$ at $C_p=7.16\times10^{-3}$ N. (□, □) $\alpha=0.5$, (○, ●) $\alpha=1.0$.

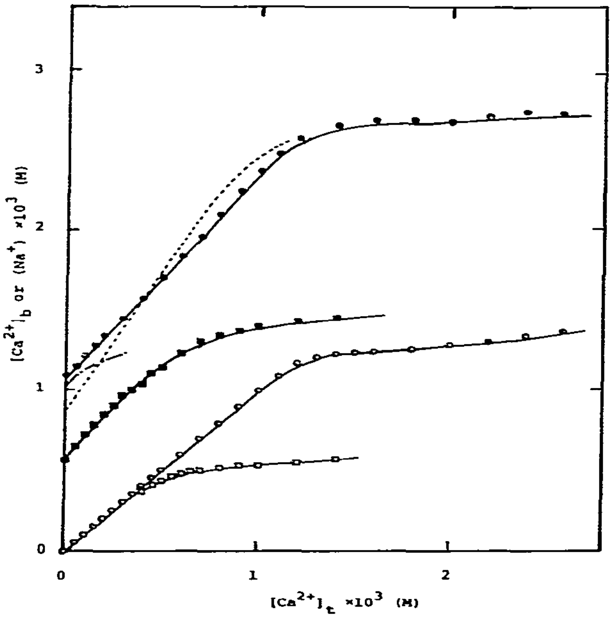

Fig. 3. Variations of (Na^+) (●, ■) and $[Ca^{2+}]_b$ (○, □) with $[Ca^{2+}]_t$ at $C_p = 2.85 \times 10^{-3}$ N. (□, ■) $\alpha = 0.5$, (○, ●) $\alpha = 1.0$.

value in the case of $[Ca^{2+}]_b$. A further addition of $CaCl_2$ beyond this concentration brings about only a small increase in (Na^+), and makes (Na^+) approach a definite value; this definite value was in fact equal to the value of Na^+ activity in a simple NaCl solution of the same concentration.

Thus, it turns out that the originally condensed Na^+ was expelled by the added Ca^{2+} being condensed on the polyion. The same types of behavior as those above are observed for more dilute polymer concentrations, $C_p = 7.16 \times 10^{-3}$, 2.85×10^{-3} and 7.16×10^{-4} N, as shown in figs. 2–4.

4. Discussion

4.1. Charge density parameter ξ_s

The charge density parameter ξ_s is the most important parameter determining the intensity of the binding of counterions for the case of cylindrical polyions in the polyelectrolyte theories. Dimensionless quantity ξ_s is defined by [1,3]

$$\xi_s = n e_0^2 / DkT, \tag{1}$$

where D, n and e_0 denote the dielectric constant, the number of charges per unit length of the polyion and the elementary charge, respectively.

The above structural charge density parameter ξ_s can be obtained from the critical concentration, C_s^0, at which Ca^{2+} condensation ceases in the process of adding $CaCl_2$ on the basis of the following relationship [1,3,12]:

$$\xi_s = \left(1 - 2C_s^0/C_p\right)^{-1}/2. \tag{2}$$

The values of ξ_s as well as of C_s^0 for several conditions determined in this way are summarized in table 1. As seen in this table, the values of ξ_s for $\alpha = 0.5$ are considerably less than half of those for $\alpha = 1.0$ in all cases. This is thought to be due to the incomplete ion condensation of the added Ca^{2+} in a low charge state such as $\alpha = 0.5$. The C_p dependence of the value of ξ_s is not clear-cut. Fairly small values have been obtained for the

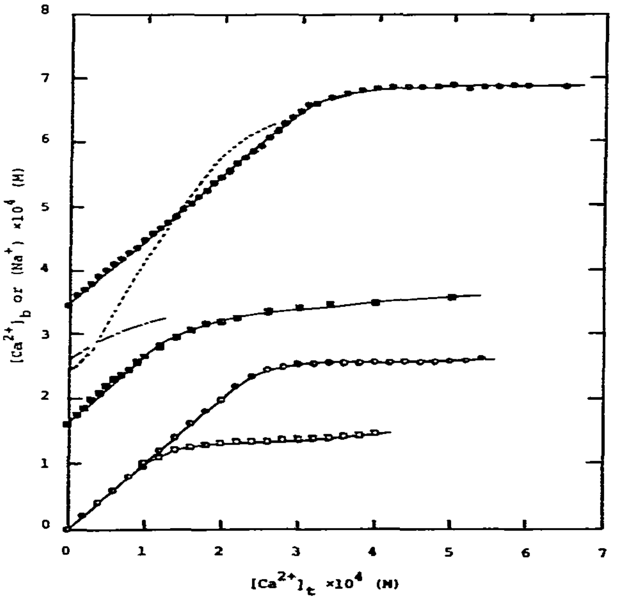

Fig. 4. Variations of (Na^+) (●, ■) and $[Ca^{2+}]_b$ (○, □) with $[Ca^{2+}]_t$ at $C_p = 7.16 \times 10^{-4}$ N. (□, ■) $\alpha = 0.5$, (○, ●) $\alpha = 1.0$.

Table 1

Values of the critical concentrations of $CaCl_2$ and the structural charge density parameter estimated from the end-points of condensation of Ca^{2+}

C_p (N)	α	C_s^0 (M)	ξ_s
7.16×10^{-4}	0.5	$(0.80\pm0.05)\times10^{-4}$	0.64 ± 0.04
	1.0	$(2.7\ \pm0.4)\times10^{-4}$	$2.0\ \pm0.3$
2.85×10^{-3}	0.5	$(0.31\pm0.01)\times10^{-3}$	0.64 ± 0.02
	1.0	$(1.11\pm0.01)\times10^{-3}$	2.26 ± 0.02
7.16×10^{-3}	0.5	$(0.78\pm0.02)\times10^{-3}$	0.64 ± 0.02
	1.0	$(2.9\ \pm0.1)\times10^{-3}$	$2.6\ \pm0.1$
4.30×10^{-2}	0.5	$(0.35\pm0.02)\times10^{-2}$	0.60 ± 0.04
	1.0	$(1.52\pm0.04)\times10^{-2}$	1.71 ± 0.04

cases of $C_p = 7.16\times10^{-4}$ and 4.30×10^{-2} N. These results seem to be due to an experimental error because of a low Na^+ concentration for the former and to the nonideal condition for the counterion condensation originating from the high polymer concentrations in the latter. The values of 2.3 and 2.6 for ξ_s obtained, however, are almost the same as the typical values of the synthetic polyelectrolytes such as poly(acrylic acid) and poly(methacrylic acid) [3,27–29].

4.2. *Analysis of the results by the counterion condensation theory*

The results of Na^+ release by the addition of Ca^{2+} were analyzed by Manning's counterion condensation theory [3]. In the absence of Ca^{2+}, the activity coefficient γ_+ of Na^+ is expressed as follows,

$$\ln\gamma_+ = -\xi_s/2,\ \xi_s < 1.0 \tag{3}$$

$$\gamma_+ = \xi_s^{-1}\,e^{-1/2},\ \xi_s > 1.0. \tag{4}$$

In the process of adding Ca^{2+}, an ionic strength effect should be introduced into the Na^+ condensation, i.e., γ_+ is written as

$$\ln\gamma_+ = -\xi X(X+2)^{-1}/2,\ \xi < 1.0 \tag{5}$$

$$\gamma_+ = \left(\xi^{-1}(X+1)(X+1)\right)^{-1} \times\exp\left[-\xi^{-1}X/2(\xi^{-1}X+2)\right],\ \xi > 1.0. \tag{6}$$

In eqs. (5) and (6),

$$X = C_p/C_s, \tag{7}$$

$$\xi = (\xi_s - 0.5)(1 - C_s/C_s^0) + 0.5, \tag{8}$$

where, C_p, C_s and C_s^0 are concentrations on the normal scale of dissociated carboxyl groups, of added $CaCl_2$ and the critical concentration on the normal scale of $CaCl_2$ at which the Ca^{2+} condensation as well as Na^+ release cease, respectively.

It should be noted that eq. (8) means that the effective charge density parameter ξ decreases linearly with increase in C_s and then reaches a value of 0.5 at $C_s = C_s^0$ at which Ca^{2+} condensation ceases. That is, it is assumed that all the Ca^{2+} added is bound to and masks the charged groups on polyions up to the critical concentration C_s^0 of $CaCl_2$. The experimental results for Ca^{2+} activity also indicate that probably all the Ca^{2+} is condensed completely to the polyions up to the critical concentration of $CaCl_2$. The degree of Na^+ binding is determined theoretically by the effective charge density parameter in the process of adding $CaCl^2$.

The activity of Na^+ in the process of Na^+ release by adding $CaCl_2$ was calculated using eq. (3) or (4) and eq. (5) or (6) with the value of ξ_s experimentally obtained for each condition. The calculated values are indicated in figs. 1–4 for $\alpha = 1.0$ (— — —) and $\alpha = 0.5$ (–·–·–). These results show that fairly good agreement between experimental and calculated values is obtained in the case of $\alpha = 1.0$ for all C_p. In particular, remarkably good results are obtained for $C_p = 2.85\times10^{-3}$ and 7.16×10^{-3} N. As described above, an agreement not quite as good as that of the previous examples for $C_p = 4.30\times10^{-2}$ and 7.16×10^{-4} N may be due to the lack of correct values of ξ_s for these C_p because of the high polymer concentration and the experimental error, respectively.

The obtained values of ξ_s in the case of $\alpha = 0.5$ are extremely small, which is attributable to the incomplete ion condensation at low charge states. As a result, the calculated values become much larger compared with the experimental values as shown in the figures.

4.3. α dependence of activity coefficient of Ca^{2+}

Next, we discuss the Ca^{2+} binding in the process of neutralization with $Ca(OH)_2$. The dependence of the activity coefficient γ_{++} of Ca^{2+} on the degree of neutralization by $Ca(OH)_2$, α, experimentally obtained in salt-free solutions at $C_p = 7.16 \times 10^{-4}$ and 7.16×10^{-3} N is shown in fig. 5. If the interaction between Ca^{2+} and the polyion is only electrostatic, γ_{++} of this system may be calculated from Manning's theory or Oosawa's theory based on the condensation hypothesis [1,3].

According to Manning's treatment [3], γ_{++} for $\xi_{\text{eff}} > 0.5$ is given by

$$\ln \gamma_{++} = -1/2 - \ln(2\alpha \cdot \xi_s), \tag{9}$$

where ξ_{eff} is the effective charge density parameter defined as $\xi_{\text{eff}} = \alpha \cdot \xi_s$.

The theoretical values of γ_{++} shown also in fig. 5 in comparison with experimental values are calculated from eq. (9) with $\xi_s = 2.0$ and 2.6 for $C_p = 7.16 \times 10^{-4}$ and 7.16×10^{-3} N. The agreement between the calculations and the experiments is very good, particularly in the range $0.5 \leqslant \alpha \leqslant 1.0$. It should be noted that the activity coefficients γ_{++} of Ca^{2+} due to the direct measurements coincide with those estimated from eq. (2) even if the latter values are for salt-containing solutions.

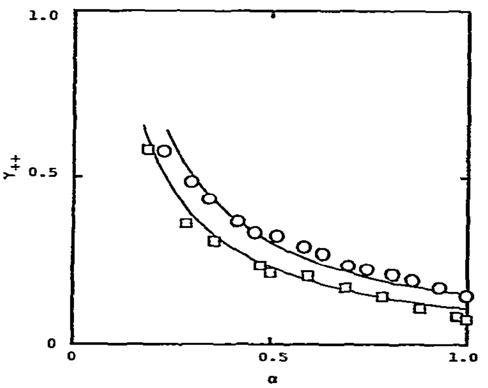

Fig. 5. Dependence of the activity coefficients of Ca^{2+}, γ_{++}, on the degree of neutralization α in salt-free MAEVE solutions at $C_p = 7.16 \times 10^{-4}$ N (○) and $C_p = 7.16 \times 10^{-3}$ N (□). Curves in the figure are theoretical values: upper curve, $\xi_s = 2.0$ and lower curve, $\xi_s = 2.6$.

As mentioned in section 1, it has been observed that when MA-copolymers are titrated with bases, the titration curves exhibit a two-step dissociation behavior. The difference between the intrinsic pK values (p$K_{0,1}$ and p$K_{0,2}$) of the two carboxyl groups is above 2 units even in the presence of divalent cations as shown in fig. 6. These results mean that one of a pair of the adjoining carboxyl groups remains unionized below the half-neutralization point even if titrated with bases of divalent cations. It was presumed previously that there were two states in the binding of divalent cations to MA-copolymers, depending on the degree of neutralization: the purely electrostatic binding around the ionized carboxyl groups at $0 \leqslant \alpha \leqslant 0.5$ and the specific binding to the pair of the adjoining carboxyl groups at $0.5 \leqslant \alpha \leqslant 1.0$ [23]. Our results in this study seem to be consistent, at least phenomenologically, with the above-mentioned re-

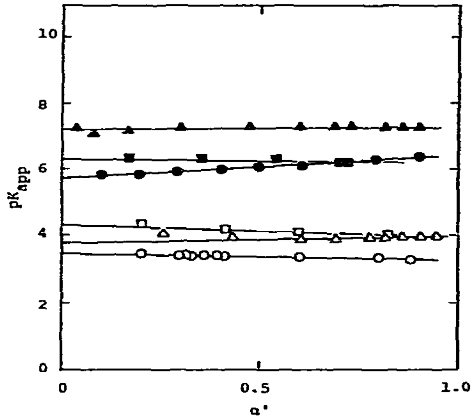

Fig. 6. Dependence of the apparent pK values on degree of neutralization α' for each dissociating group in the solutions of MA-copolymers which are neutralized with the bases of divalent cations: (△, ▲) solution of MAEVE neutralized with $Ba(OH)_2$ in the presence of 0.37 M NaCl at $C_p = 2.0 \times 10^{-3}$ N; (□, ■) salt-free solution of MAEVE neutralized with $Ca(OH)_2$ at $C_p = 7.5 \times 10^{-4}$ N; (○, ●) solution of MAE (copolymer of maleic acid and ethylene) neutralized with $Ba(OH)_2$ in the presence of 1 M NaCl at $C_p = 1.8 \times 10^{-2}$ N. Intrinsic pK values (p$K_{0,1}$, p$K_{0,2}$) are obtained from the intercepts at $\alpha' = 0$ by extrapolation.

sults, although no certain reason exists to distinguish the binding character of Ca^{2+} to this polyion between $0 \leqslant \alpha \leqslant 0.5$ and $0.5 \leqslant \alpha \leqslant 1.0$.

Acknowledgments

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