ELSEVIER

PII: S0032-3861(97)00291-7

Polymer Vol. 39 No. 2, pp. 437–440, 1998

0032-3861/97/$17.00+0.00

Divalent counterion binding of Na poly(α-hydroxy acrylate)

Kenji Ogawara, Shunsuke Kawazoe, Toru Tamura, Susumu Kawauchi, Mitsuru Satoh* and Jiro Komiyama
Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan
(Received 15 November 1996)

Divalent counterion binding has been investigated for Na poly(α-hydroxy acrylate) (PHANa) in the presence of $MgCl_2$, $CaCl_2$, or $BaCl_2$ by measuring the reduced viscosity, apparent turbidity and divalent counterion activity of the pertinent aqueous solutions. It was found that the viscosity decreases in the order, $Mg^{2+} \gg Ba^{2+} \geq Ca^{2+}$, while the turbidity at the devalent counterion ratio to the polymer, $C_2/C_p \sim 0.5$, was in the order, $Mg^{2+} > Ca^{2+} \geq Ba^{2+}$. The former order proved to be consistent with that from the activity measurement. The apparent contradiction suggested by the result of the turbidity measurement has been interpreted in terms of 'hydration force'. Reference experiments with Na poly(acrylate) (PAANa) demonstrated that PHANa is able to bind Ca^{2+} over Mg^{2+} much more effectively than PAANa, probably through coordination of the α-hdyroxyl group to the former counterion. © 1997 Elsevier Science Ltd.

(Keywords: polyelectrolyte; counterion binding; hydration)

INTRODUCTION

Counterion binding of polyelectrolyte has been extensively studied for several decades, by theoretical[1] and experimental[2] approaches, while it is still providing us with interesting and enigmatic behaviors to be challenged for elucidation. Recently, Iida found that activity of Ca^{2+} in aqueous poly(acrylic acid) (PAA) solution at low degree of neutralization was increased by adding small amounts of KCl, while it decreased with further addition of the salt[3]. This observation may be of relevance to Ca^{2+} ion control in biosystems. Besides this example, many researchers have reported on polyelectrolyte specificities which may be ascribed to conformational change and intramolecular interaction: conformational transition of PAA in methanol and its counterion specificity[4], two-step dissociation of polycarboxylates such as poly(itaconic acid)[5] and more generally so-called coil-globule transition[6].

Poly(α-hydroxy acrylic acid) (PHA) is an interesting polyelectrolyte, which forms lactone rings with addition of proton, as reported in our previous paper[7]. PHA has been known since 1940[8] and utilized as an efficient stabilizer of hydrogen peroxide in aqueous solution. Since H_2O_2 is easily decomposed in the presence of divalent cations such as Mn^{2+}, PHA is used as the stabilizer because of its high ability for divalent counterion binding. Besides these empirical observations, however, the physico-chemical properties of PHA in aqueous solution has been poorly investigated so far.

In the present paper, we performed a comparative study of PHA and PAA for their divalent counterion binding by measuring the reduced viscosity, apparent turbidity and activity of Mg^{2+} and Ca^{2+} in the pertinent aqueous solutions. The last experimental data were analyzed with a counterion condensation theory[9] to estimate the relative binding strength, and thus we attempted to clarify the role of the α-hdyroxyl group of PHA in counterion binding.

EXPERIMENTAL

Samples

Sodium poly(α-hydroxy acrylate) (PHANa) ($M_w = 7.3 \times 10^4$ for lot 1 and 5.9×10^4 for lot 2) was kindly supplied by Nippon Peroxide Co. Ltd. PAANa ($M_w = 6.0 \times 10^4$) was purchased from Poly Science. These polymer samples were purified by ultrafiltration with UP-20 membrane (Toyo Roshi) and then collected by freeze-drying.

NaCl, $MgCl_2$, $CaCl_2$, and $BaCl_2$ of analytical grade were purchased from Nacalei Tesque. Deionized and distilled water was used throughout the experiment.

Viscosity measurement

Sample solutions were prepared as follows: each polymer solution (lot 1 sample was used as PHANa sample) of 1.0×10^{-1} basemol dm^{-3} was put in a volumetric flask (20 ml) and then mixed with distilled water and salt solution 1.0×10^{-1} M to adjust the final polymer concentration, C_p, to 1.0×10^{-2} basemol dm^{-3}, and the salt to polymer ratio, C_2/C_p, to 0.20–0.38 (C_s/C_p for NaCl to 0.40–0.76 of the same ionic strength as those for the divalent counterion systems). The reduced viscosity was measured with an Ostwald viscometer (capillary diameter = 0.5 mm) at 25.0 ± 0.005°C.

Turbidity measurement

Apparent turbidities of PHANa (lot 2) and PAANa solutions in the presence of one of the three divalent counterions, Mg^{2+}, Ca^{2+} or Ba^{2+}, were estimated as absorbance at 600 nm at 25 ± 0.5°C. The sample solutions were prepared in a volumetric flask of 50 ml, in which 5 ml

---

* To whom correspondence should be addressed

of polymer solution (0.1 basemol dm^{-3}) and the required amount of water, and finally a salt solution of 1.0 × 10^{-2} M were added under vigorous stirring to adjust C_2/C_p to 0.40–0.60. The relatively low concentration of salt solutions used for the sample preparation was necessary to prevent the polymers from precipitating around at $C_2/C_p = 0.4$.

Activity measurement

Apparent activities of Mg^{2+} and Ca^{2+} in PHANa (lot 1) and PAANa solutions were estimated by a calibration method. The calibration was made twice, before and after each measurement. Linearity of the calibration curves plotted as electromotive force (e.m.f.) vs. divalent counterion activities which were estimated by an extended Debye Hückel equation[10], was satisfactory and the reproducibility of the respective e.m.f. values were within ±5%.

E.m.f. was measured with an Orion 901 Ion-analyser by using a divalent counterion electrode (Orion 93-32) and a double junction reference electrode (Orion 90-02) at 25.0 ± 0.058C. C_p was fixed at 1.0 × 10^{-2} basemol dm^{-3} and C_2/C_p was varied as 0.302–0.376.

RESULTS AND DISCUSSION

Viscosity measurement

Figure 1(a) and *Figure 1*(b) show the reduced viscosities of PHANa and PAANa solutions, respectively, plotted against $I^{-1/2}$. Here I is the ionic strength which was calculated by assuming that all the added divalent counterions are bound to polymer to exchange with two equivalent Na ions. As a general trend, it is seen that η_{sp}/C_p decreases with decreasing (increasing) $I^{-1/2}$ (salt concentration or I), a natural manifestation of ionic screening of electrostatic repulsion of polymer-changed groups. Here one should note the remarkable counterion specificities in the viscosity, $Na^+ \gg Mg^{2+} \gg Ba^{2+} \geq Ca^{2+}$ for PHANa and $Na^+ \gg Mg^{2+} > Ca^{2+} > Ba^{2+}$ for PAANa. Since the differences in η_{sp}/C_p at the same ionic strength may be ascribed to those in counterion binding degree, these experimental results suggest that PHA discriminates Ca^{2+} and Mg^{2+} much more effectively than PAA. This may be seen more directly in *Figure 2*, where a ratio of η_{sp}/C_p of the divalent counterion systems to that of NaCl was plotted for both the polymers, to show effects from divalent counterion binding by eliminating those from the difference in the molecular weight of the polymer samples. According to the plots, the binding degrees should be higher in the order, Mg^{2+} (PAA) ≤ Mg^{2+} (PHA) < Ca^{2+} (PAA) < Ba^{2+} (PAA) ≪ Ba^{2+} (PHA) ≤ Ca^{2+} (PHA). The ratios of the viscosity ratio between Ca^{2+} and Mg^{2+} are ca. 2.7 and 16 for PHA at $I^{-1/2} = 15.8$ and 11.5 ($C_2/C_p = 0.2$ and 0.38), respectively, while those for PAA are only 1.2 and 1.8, respectively. Although these values do not quantitatively correspond to the ratio of the binding degrees, they strongly suggest that Ca^{2+} and Ba^{2+} are specifically bound onto PHA, probably through coordination of the α-hydroxyl group to the counterions.

Activity measurement

The logarithm of apparent activities obtained for the divalent counterions (Mg^{2+} and Ca^{2+}) was plotted against C_2/C_p in *Figure 3*. The activities indicate that the binding degree of the divalent counterions in the two aqueous polymer solutions are in the order, Mg^{2+} (PHA) < Mg^{2+} (PAA) < Ca^{2+} (PAA) < Ca^{2+} (PHA). The order of Ca^{2+} is in agreement with that from viscosity, while not for Mg^{2+} systems. The apparent contradiction may be explained by taking a count of intramolecular hydrogen bonding between OH and COO$^-$ on PHA. The existence of such hydrogen bonding for PHANa has been suggested by Tamura et al.[7], who investigated conformation of PHANa in aqueous solution with IR spectroscopy and ab initio calculation. The intramolecular hydrogen bonding should reduce the site binding strength of the pertinent divalent counterions to some extent, because the counterions need to break the hydrogen bond to be bound to the polymer charge. However, if a free OH group coordinates to the bound counterion, then it may contribute to the stabilization of the bound state. This seems to be the case for PHANa/Ca^{2+} system, actually the lower activity of Ca^{2+} than in the PAANa system must be ascribed to the coordination of the α-hdyroxyl group. With a similar reasoning, the result on PHANa/Mg^{2+} system may be interpreted; the coordination of OH to bound Mg^{2+} is not so effective in compensating

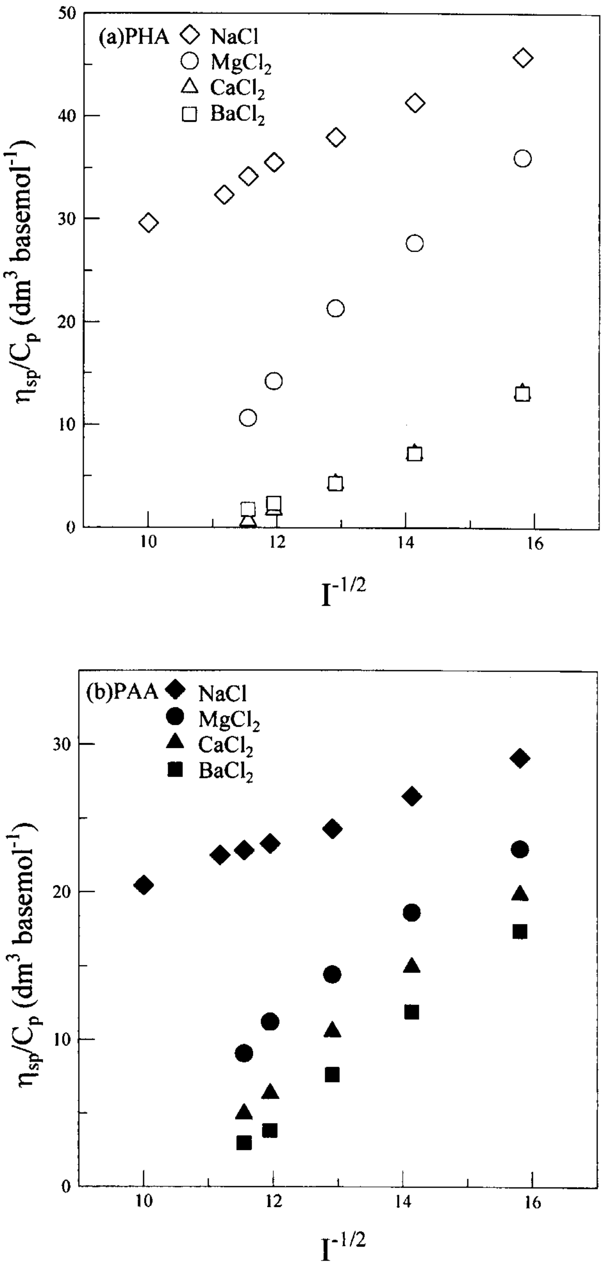

Figure 1 Dependence of the reduced viscosity on $I^{-1/2}$. (a) PHA; (b) PAA

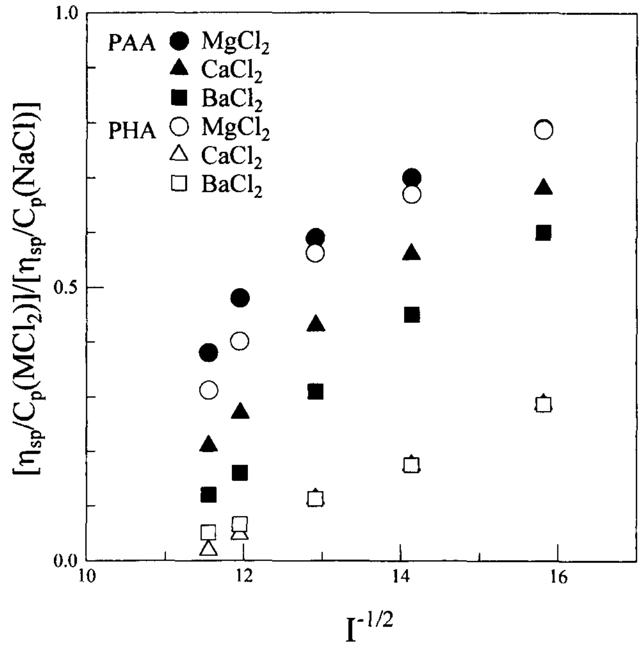

Figure 2 Comparison of the reduced viscositites of PHA and PAA systems

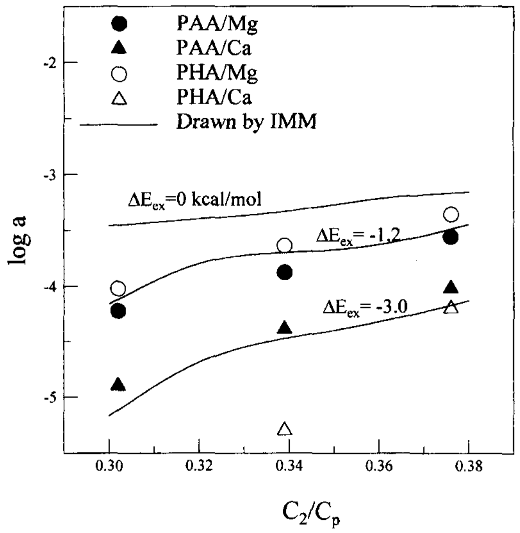

Figure 3 Apparent turbidity of PHA and PAA solutions in the presence of divalent counterions

Table 1 Extra-interaction energy (ΔE_{ex}) and degrees of counterion binding estimated for C_2/C_p = 0.376 by IMM

System	ΔE_{ex} (kcal/mol)	Binding degree of Na^+	Binding degree of Mg^{2+} or Ca^{2+}	Effective polymer charge fraction
PAA/Mg	−1.5	0.071	0.328	0.273
PHA/Mg	−0.84	0.097	0.315	0.273
PAA/Ca	−2.8	0.044	0.365	0.226
PHA/Ca	−3.1	0.039	0.370	0.221

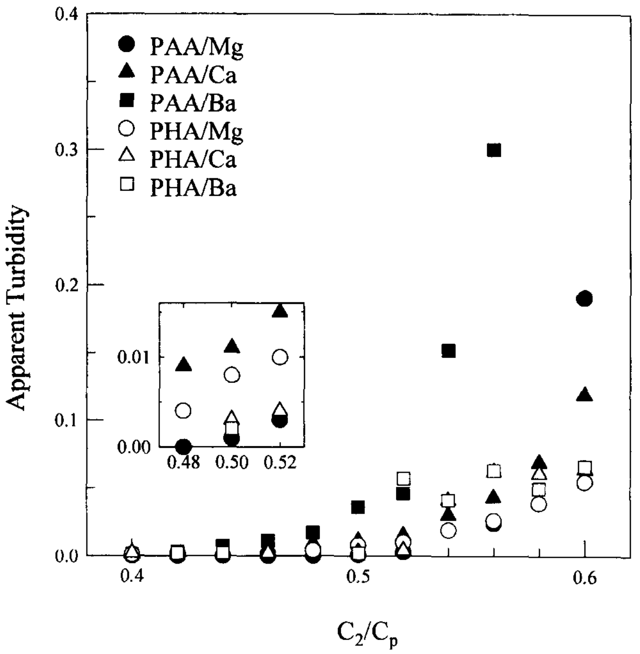

Figure 4 Activities (log *a*) of Mg^{2+} and Ca^{2+} in PHA and PAA solutions

the energy necessary for breaking the hydrogen bond, while it is sufficient to reduce the polymer dimension (as opposed to PAANa) in the presence of Mg^{2+}. The supposed difference in the coordination of OH group to Mg^{2+} and Ca^{2+} cations may be rationalized in terms of differences in the ion sizes and hydration energies; the enthalpically optimum binding state of the former ion, which has smaller size and higher hydration energy, should be accompanied by an unfavourable entropy change; in other words, tight and close coordination is necessary to compensate the unfavorable dehydration energy.

The solid curves in the figure were drawn according to our counterion condensation model (Intermediate Model, IMM)[9], which have been successfully utilized to estimate counterion binding degrees and activities in polyelectrolyte systems of condensation mode[9], as well as in those of site binding[11-13]. In the latter case, extra interaction energy, ΔE_{ex}, has been incorporated in the free energy minimization condition to fit the experimental activity data. The three curves in the figure were thus obtained with $\Delta E_{ex} = 0$, -1.2 and -3.0 kcal/mol, the latter two of them reproducing the dependence of log *a* on C_2/C_p. ΔE_{ex} values which were estimated by fitting to experimental activities at $C_2/C_p = 0.376$ are given in *Table 1*. The value of PAA/Mg^{2+}, -1.5 kcal/mol, is in a good agreement with -1.2 kcal/mol estimated in a previous study[11], while that for Ca^{2+}, -2.8 kcal/mol, is rather smaller than the previous value, -3.9 kcal/mol. Although this discrepancy cannot be fully explained at the present stage, it may be ascribed to the higher polymer concentration, 0.025 basemol dm^{-3}, used in the previous study[11].

The counterion binding analysis based upon the theoretical model will be utilized in the last section.

Turbidity measurement

Turbidity was used as a measure of counterion binding in the present polyelectrolyte systems because the strong binding of divalent counterions to polycarboxylates should be accompanied by substantial dehydration which must reduce the solubility of the polymer in water. However, the experimental results, as given in *Figure 4*, show us a puzzle for the order of turbidity. For example, at around C_2/C_p = 0.5 (we confine our discussion on turbidity to the relatively lower C_2/C_p region because of the scatter of the data in the higher C_2 region), the apparent turbidity (absorption at

600 nm) increases as; PAA/Mg $\leq$ PHA/Ba $\leq$ PHA/Ca $<$ PHA/Mg $<$ PAA/Ca $\ll$ PAA/Ba. This order suggests an order of counterion binding strength, while it contradicts those between the two Mg^{2+} systems, two Ca^{2+} systems and also between PHAMg and Ca, obtained from the activity measurements.

Here we invoke 'hydration force'[14] in order to interpret the results on turbidity. Hydration force contributes to stabilization of colloidal particles, since large dehydration energy is necessary for coagulation of hydrophilic surfaces. For example, it is known that an ampholytic polystyrene latex at the isoelectric point is stable even in concentrated salt solutions of LiCl or KCl while not in CsCl[15]. This is interpreted as being caused by the hydration force imparted to the latex by the former small cations bound on the surface. In the present case, hydration force must depend on the monovalent and the divalent counterion binding degree; since hydration energies of divalent counterions are much larger than those of monovalent ones, higher divalent counterion binding and lower monovalent binding may resist polymer precipitation more effectively than a case of lower divalent binding and higher monovalent binding. Thus, we estimated the respective binding degrees in PHANa and PAANa systems with IMM based on the experimental activity data. The results are shown in *Table 1*. In the presence of Mg^{2+} of 3.76×10^{-3} M, the binding degree of Na^+ in PHANa system is larger by ca. 40% than that in PAANa, suggesting that more aggregation sites are available on the PHANa. A similar reasoning may be appropriate for the order between PHA/Mg and Ca.

On the other hand, in the presence of Ca^{2+}, PHA binds less Na^+ only by ca. 10% than PAA. Although 'hydration force' suggests that PAANa/Ca aggregates more easily than PHANa/Ca, it is not certain whether the experimental order in the turbidity, PHA/Ca $<$ PAA/Ca, is originated only from the difference in the 'hydration force'. Other factors, for example, the strong contraction of the PHANa chain in the presence of Ca^{2+}, which has been suggested by the reduced viscosity, may retard the growth of aggregation.

In conclusion, we have found that PHA has a much higher ability to discriminate Ca^{2+} over Mg^{2+} in the counterion binding, and ascribed the ability to effective coordination of the α-OH group to the former ion. The experimental results on the apparent activity and the reduced viscosity were consistently interpreted, while the apparent turbidity turned out to be not directly correlated with the counterion binding degrees.

It should be noted that the counterion-specificity observed in the present study may be valid only at neutral pH. As stated in Section Section 1, PHA assumes intramolecularly lactone rings with consumption of the hydroxyl groups under acidic conditions. The titration behavior and divalent counterion binding of PHA in the presence of acid are now being investigated.

ACKNOWLEDGEMENTS

We thank Nippon Peroxide Co., Ltd., for the generous supply of PHANa samples which made this work possible.

REFERENCES

1. Manning, G.S., *Chem. Phys.*, 1969, **51**, 924.
2. Ikegami, A. and Imai, N., *J. Polym. Sci.*, 1962, **56**, 133.
3. Iida, S., *Biophys. Chem.*, 1996, **57**, 133.
4. Klooster, N.Th.M., van der Touw, F. and Mandel, M., *Macromolecules*, 1984, **17**, 2070.
5. Kawaguchi, S., Nishikawa, Y., Kitano, T., Ito, K. and Minakata, A., *Macromolecules*, 1990, **23**, 2710.
6. Khokhlov, A.R., *J. Phys. A: Math. Gen.*, 1980, **13**, 979.
7. T. Tamura, S. Kawauchi, M. Satoh, J. Komiyama, Polymer, 1997, **38**, 2093.
8. Marvel, C.S., Dec, J., Cooke, H.G. Jr. and Cowan, J.C., *J. Am. Chem. Soc.*, 1940, **62**, 3495.
9. Satoh, M., Kawashima, T. and Komiyama, J., *Biophys. Chem.*, 1988, **31**, 209.
10. Kielland, J., *J. Am. Chem. Soc.*, 1937, **59**, 1675.
11. Satoh, M., Hayashi, M., Komiyama, J. and Iijima, T., *Polymer*, 1990, **31**, 501.
12. Satoh, M., Yoda, E. and Komiyama, J., *Macromolecules*, 1991, **24**, 1123.
13. Miura, S., Satoh, M. and Komiyama, J., *Polymer*, 1996, **37**, 1641.
14. H. van Olpen, An Introduction of Clay Colloid Chemistry, Ch. 10, Wiley, New York, 1997.
15. Healy, T.W., Chan, D. and White, L.R., *Faraday Discuss. Chem. Soc.*, 1978, **65**, 156.