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RAMAN SPECTROSCOPIC STUDIES ON THE INTERACTION BETWEEN DIVALENT COUNTERION AND POLYION

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The nature of the interaction between polyacrylate ion and several divalent cations, such as Cu^{2+}, Mn^{2+}, Zn^{2+}, Ba^{2+} and Mg^{2+}, was investigated using Raman spectroscopy. A specific Raman band characteristic of a carboxyl group is shifted upon addition of Cu^{2+}, Zn^{2+} and Mn^{2+} to partially neutralized poly(acrylic acid). On the other hand, no frequency shift of the specific Raman band is observed on addition of Mg^{2+} and Ba^{2+}, though the intensity of the specific Raman band decreases with concentration of $MgCl_2$. It is concluded from these Raman data that the interaction between polyacrylate ion and Cu^{2+}, Zn^{2+} or Mn^{2+} includes a specific interaction with bond formation, whereas in the case of Mg^{2+} and Ba^{2+}, the electrostatic interaction is dominant.

1. Introduction

The interaction between counterions and fixed charged groups of polyelectrolytes, which is often discussed in studying physical properties of polyelectrolyte solutions, may be classified into a few groups [1]. One is specific ion binding and the other is ionic atmosphere formation around polyions, including ion pair formation.

In a previous paper [2], we confirmed using Raman spectroscopy that the nature of the interaction between polyacrylate ion and several alkali metal ions is simply electrostatic, in agreement with previous conclusions [3,4]. On the other hand, it was found by several investigators that the interaction between poly(acrylic acid) and Cu^{2+} is a specific one with bond formation. Wall [5], Morawetz [6,7] and Gregor et al. [8] found a strong absorption peak in the ultraviolet absorption spectra of poly(acrylic acid) solution when Cu^{2+} was added to the solution. However, except for Cu^{2+}, the nature of the binding of the other divalent cations on polyacrylate ion is not absolutely clear.

The interaction of various divalent cations with poly(acrylic acid) have been investigated using various experimental methods, such as polarography [9], potentiometry, [3,10,11], NMR [12–16] and infrared absorption [17,18]. Mandel [3] obtained potentiometric titration curves of poly (acrylic acid) in the presence of many kinds of divalent ions, such as Cu^{2+}, Co^{2+}, Ni^{2+} and Ba^{2+}, and reported that Cu^{2+} shows a clearly different behavior from that of the other divalent ions. Leyte et al. [12,13] reported that no evidence for direct site binding between poly(acrylic acid) and Mn^{2+} was found in their NMR study, and, hence, Mn^{2+} associated with the polyelectrolyte may be fully hydrated. On the other hand, Weill et al. [15,16] asserted from their NMR measurement that Mn^{2+} is bound to polyacrylate ion above the degree of neutralization of 30%. Moreover, it may

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be certain that no specific interaction exists between polyacrylate ion and alkali earth metal ions [17,18].

Raman spectroscopy is one of the most powerful methods for investigating such interactions. Specific complex formation can be detected from the appearance of a new Raman band or from shifts of specific Raman bands [19]. Raman spectroscopy cannot clearly distinguish between the ion atmosphere interaction and ion pair formation, but the intensity and half-width of the Raman band relating to the fixed charged group may be varied if counterions approach the fixed charged group as closely as they can affect its bond polarizability. Raman spectroscopy was applied to the study of complex formation between $-COO^-$ and divalent cations in simple electrolyte solutions [19]. Fujita et al. [20] reported complex formation of not only Cu^{2+} but also some other divalent metal ions with oxalate ion. However, Raman spectroscopy has not yet been applied to the study of the interaction between divalent ions and polyelectrolyte.

2. Experimental

2.1. Samples

Poly(acrylic acid) samples used were the same as those described in our previous work [2]. They were commercially supplied from Scientific Polymer Products, Inc. Their molecular weights were 1.8×10^3 and 9.0×10^4, respectively. All simple salts added to poly(acrylic acid) solutions, viz., sulfates, nitrates and perchlorates of various divalent cations, were of guaranteed reagent grade and were used without further purification. All aqueous solutions were prepared using deionized water.

2.2. Raman spectroscopy

The Raman spectra of poly(acrylic acid) were measured with a double monochromatic laser Raman spectrometer JRS-U1 (Japan Electron Optic Laboratory Co., Ltd.) and an argon ion laser operating at 488 nm (Coherent Radiation Co., Ltd.) [2]. All measurements were carried out in

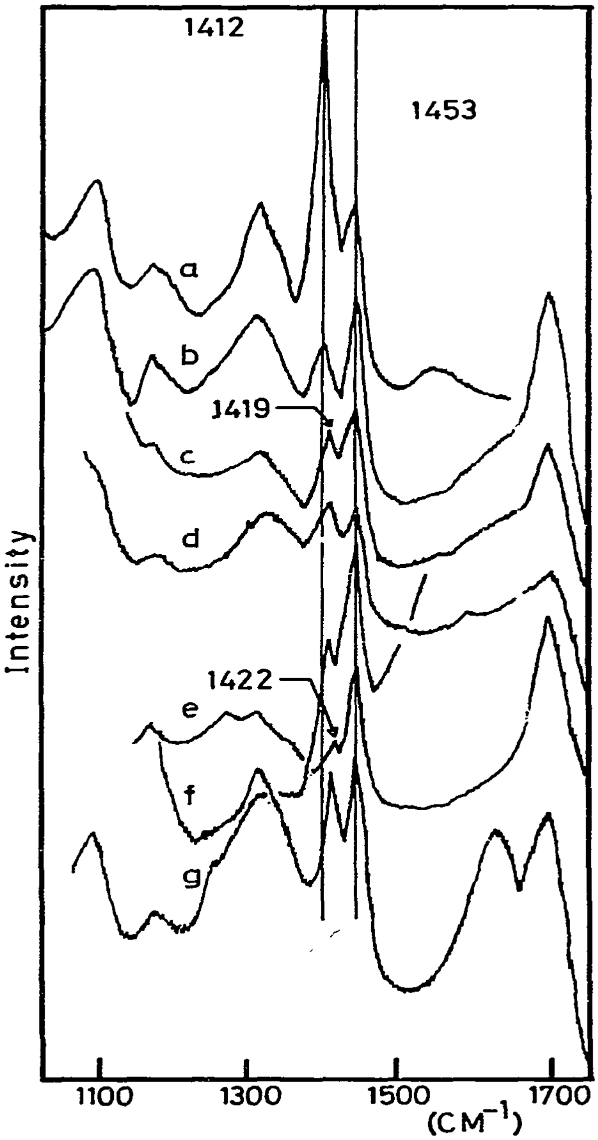

Fig. 1. Raman spectra of poly(acrylic acid) (e), sodium polyacrylate (a) and 20% neutralized poly(acrylic acid) in the presence of different cupric salts (b–d, f and g). Added salts: (b) no salt, (c) 0.5 mol/l $Cu(ClO_4)_2$, (d) 1.0 mol/l $Cu(NO_3)_2$, (f) 0.5 mol/l $Cu(ClO_4)_2$, (g) 0.5 mol/l $CuSO_4$. Molecular weight of poly(acrylic acid): 1.8×10^3 except in trace f (9.0×10^4). The concentration of poly(acrylic acid) was 2.0 mol/l except in trace f (0.67 mol/l).

pure aqueous solutions at room temperature. The polymer concentrations in most experiments were 2.0 or 1.0 mol/l with respect to acrylate monomer. The samples were usually neutralized with NaOH to a degree of 20 or 30% and aqueous solutions of various salts of divalent cations were added to their solutions. Precipitation easily occurs if the concentration of added salt is increased. In most experiments, the degree of neutralization of poly(acrylic acid), α, could not be increased beyond $\alpha = 0.3$ because of the constraints concerning the solubility and sensitivity of the instrument. It is usually believed that the degree of neutralization, $\alpha = 0.2$, corresponds to the threshold for counterion binding. The added salts were added slightly in excess of the concentration of $-COO^-$ if $\alpha = 0.2$, but addition could not be done beyond half of the concentration of $-COO^-$ if $\alpha = 0.3$.

2.3. Potentiometric titration

The pH measurement of solutions was carried out by using a model 701A digital pH meter manufactured by Orion Research, Inc. The sensitivity of the instrument is 0.001 pH unit. The titration was carried out at 25.0 ± 0.1°C using a standard 0.1 N NaOH solution delivered with a microburet. The solutions for titration measurements contained 4.9×10^{-3} mol/l poly(acrylic acid), 1.0×10^{-2} mol/l KCl and 5.0×10^{-4} mol/l divalent cation.

2.4. Ultraviolet spectroscopy

The ultraviolet absorption spectra were obtained with a Union Giken SM-401 spectrophotometer.

3. Results

3.1. Raman spectroscopy

The stretching vibrational mode of a metal-oxygen bond is usually observed in the frequency region from 300 to 500 cm^{-1}. However, the Raman spectrum below 1000 cm^{-1} overlaps with those of the aquo complexes of divalent cations and also with those of poly(acrylic acid). Therefore, we draw attention to the Raman band char-

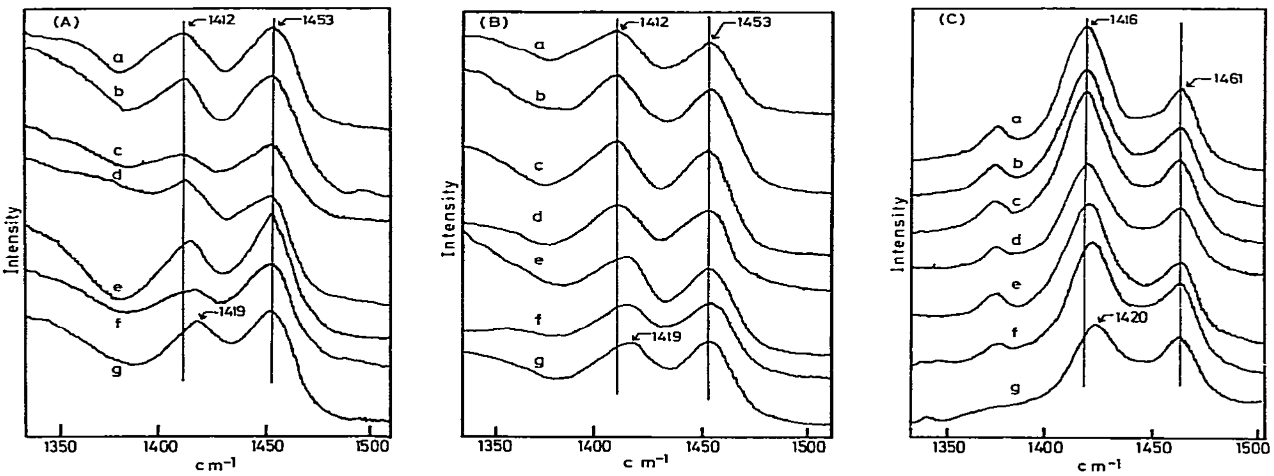

Fig. 2. Raman spectra of 20 and 30% neutralized poly(acrylic acid) (A and B), and 40% neutralized propionic acid (C) in the presence of different divalent salts. Added salts: (a) no salt, (b) $Mg(ClO_4)_2$, (c) $Ba(ClO_4)_2$, (d) $NiSO_4$, (e) $MnCl_2$, (f) $Zn(ClO_4)_2$, (g) $Cu(ClO_4)$. The concentrations of added salts were 0.5 mol/l for 20% neutralized poly(acrylic acid) of 2.0 mol/l and propionic acid of 2.0 mol/l, and 0.075 mol/l for 30% neutralized poly(acrylic acid) of 1.0 mol/l.

acteristic of the $-COO^-$ group which is located at 1412 cm^{-1}. The detailed assignment of the Raman spectra of poly(acrylic acid) is given in a previous paper [2].

Fig. 1 shows the Raman spectra of 20% neutralized poly(acrylic acid) in the presence of Cu^{2+}, in comparison with those of poly(acrylic acid), 20% neutralized poly(acrylic acid) and sodium polyacrylate. The Raman band at 1412 cm^{-1} shifts to the higher frequency side by 7 cm^{-1} if an amount of cupric perchlorate is added to 20% neutralized poly(acrylic acid) solution. The same frequency shift is observed for both cupric sulfate and nitrate, and also for a different poly(acrylic acid) sample with a higher molecular weight. Fig. 2A, B and C shows the Raman spectra of partially neutralized poly(acrylic acid) solutions and those of partially neutralized propionic acid solutions, containing various divalent cations, respectively. The specific Raman band located at 1412 cm^{-1} is shifted with addition of Cu^{2+}, Mn^{2+} and Zn^{2+}, whereas no shift is observed with addition of Mg^{2+}, Ba^{2+} and Ni^{2+} in both Fig. 2A and B. Moreover, entirely the same tendency is observed for both poly(acrylic acid) and propionic acid solutions. Therefore, it can be concluded that the frequency shifts are due to complex formation between divalent cations and the $-COO^-$ group.

The Raman spectrum of fully neutralized sodium polyacrylate containing $MgCl_2$ is compared with that containing NaCl in fig. 3. As was done in a previous paper [2], the Raman intensity ratio, R, of two bands located at 1412 and 1453 cm^{-1} ($R = I_{1412}/I_{1453}$) is plotted against the concentrations of the added salts in fig. 4. The band located at 1453 cm^{-1}, which is used as the refer-

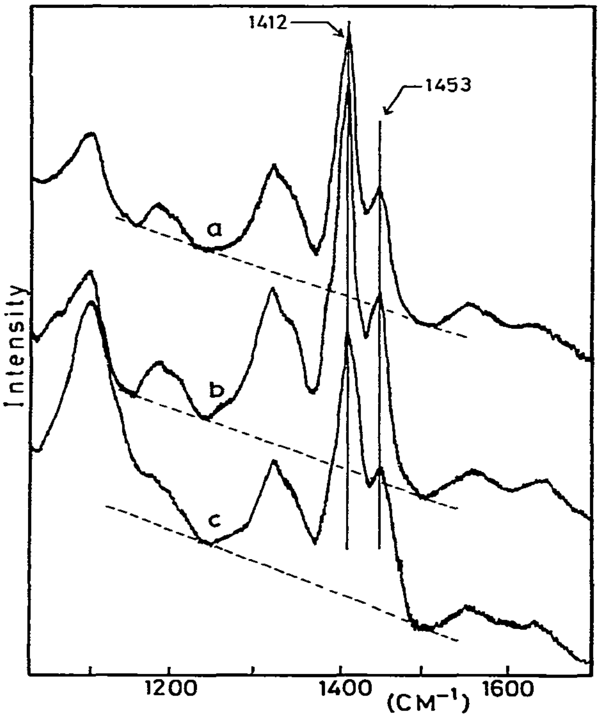

Fig. 3. Raman spectra of sodium polyacrylate on addition of NaCl and $MgCl_2$. (a) No salt. (b) NaCl. (c) $MgCl_2$. The concentration of sodium polyacrylate ($M_r = 1.8 \times 10^5$) was 2.0 mol/l.

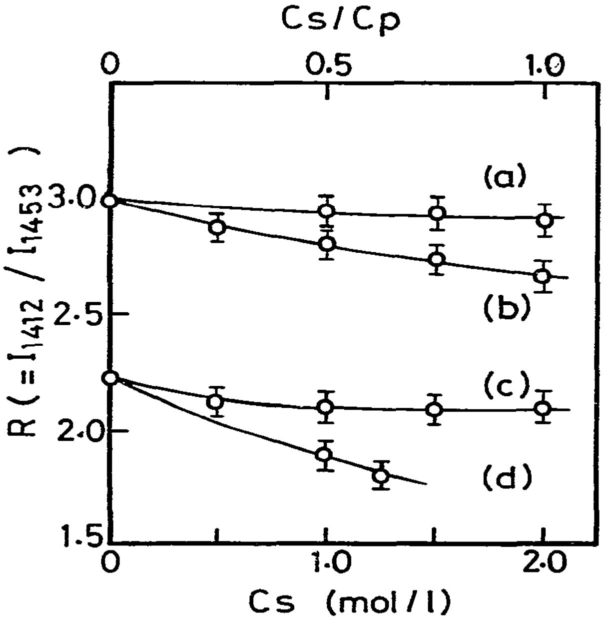

Fig. 4. The intensity ratio, R, as a function of the concentration of added salt (C_s) and the concentration ratio (C_s/C_p), where C_p is the concentration of polymer (C_p = 2.0 mol/l). (a) Sodium propionate + NaCl, (b) sodium propionate + $MgCl_2$, (c) sodium polyacrylate + NaCl, and (d) sodium polyacrylate + $MgCl_2$.

ence band, is assigned as the $-CH_2-$ bending mode [2]. The Raman intensity ratio, R, decreases more steeply with addition of $MgCl_2$ than with addition of NaCl. The same trend is observed for sodium propionate solution.

3.2. Potentiometric titration

The potentiometric titration curves of poly(acrylic acid) in the presence of divalent cations are shown in fig. 5. The curve for the solution containing Cu^{2+} is quite different from those for the solutions containing the other cations. The curves for Zn^{2+}, Mn^{2+} and Ni^{2+} are slightly different from those for Mg^{2+} and Ba^{2+}. These results are in good agreement with those obtained by Mandel [3].

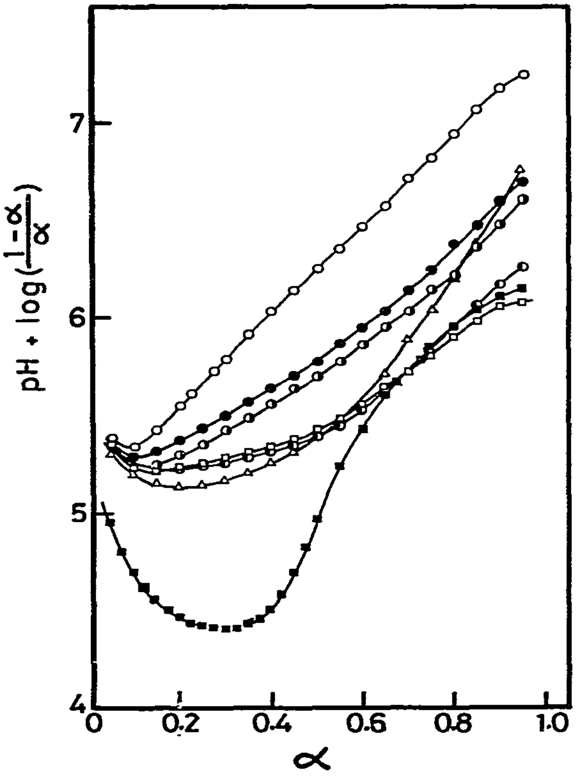

Fig. 5. Potentiometric titration curves of poly(acrylic acid) with NaOH in the presence of various divalent salts and 0.01 mol/l KCl. The degree of ionization, α, was calculated from the amount of NaOH added. Added salts (in mol/l): (○) no divalent salt; (●) 4.7×10^{-4}, $Mg(ClO_4)_2$; (○) 5.1×10^{-4}, $Ba(ClO_4)_2$; (○) 4.9×10^{-4}, $NiSO_4$; (△) 4.9×10^{-4}, $Zn(ClO_4)_2$; (□) 4.9×10^{-4}, $MnCl_2$; (■) 5.1×10^{-4}, $Cu(ClO_4)_2$. The concentration of poly(acrylic acid) was 4.9×10^{-3} mol/l and its molecular weight 9.0×10^{4}.

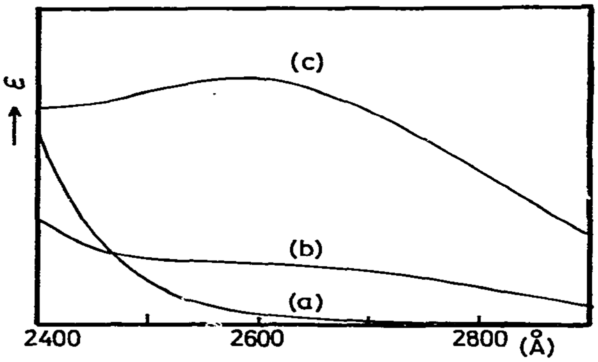

Fig. 6. Absorption spectra of 20% neutralized poly(acrylic acid) solutions. (a) 1.98×10^{-2} mol/l $Cu(ClO_4)_2$ only, (b) without $Cu(ClO_4)_2$, (c) in the presence of 4.1×10^{-4} mol/l $Cu(ClO_4)_2$. The concentration of poly(acrylic acid) was 9.1×10^{-4} mol/l and its molecular weight 9.0×10^{4}.

3.3. Ultraviolet spectra

Fig. 6 shows the ultraviolet spectra of partially neutralized poly(acrylic acid) in the presence of Cu^{2+}. The absorption observed at about 2600 Å is considered to be due to complex formation between Cu^{2+} and polyacrylate ion, as pointed out by Wall and Gill [5].

4. Discussion

From the above experimental results, it is clear, as was pointed out by many investigators, that a complex is formed between Cu^{2+} and $-COO^-$ groups in the poly(acrylic acid) chain. In the presence of Mn^{2+} and Zn^{2+} also, the shifts of a band located at 1412 cm^{-1} strongly suggest that Mn^{2+} and Zn^{2+} also form complexes with polyacrylate ion. This complex formation is not a feature of polymeric $-COO^-$ but is observed for partially neutralized propionic acid as well.

For Mg^{2+}, it is found in fig. 4 that the intensity ratio, R, decreases with increasing concentration of $MgCl_2$ if $MgCl_2$ is added to fully neutralized sodium polyacrylate. The decrease in R implies that the environmental state around $-COO^-$ is influenced by the added salt. The influence of Mg^{2+} appears to be stronger than that of Na^+ because of its higher charge. The same tendency is observed for propionic acid solution. Leyte et al. [17,18] concluded from an infrared study on poly(acrylic acid) salts in ^2H_2O solution that no nonionic interaction, such as site binding, occurs in solution for alkali metal and alkali earth metal salts of poly(acrylic acid). This conclusion agrees with our results obtained in this experiment and in our previous paper [2].

Thus, it is certain that the nature of the interaction between a polyion and Cu^{2+}, Mn^{2+} or Zn^{2+} is at least partially nonionic, while the nature of the interaction with alkali metal and alkali earth metal cations is mainly ionic. However, the interaction between a polyion and counterions may vary from being ionic to covalent, depending on the combination of the metal ion and fixed charged group.

In coordination chemistry, it is well known that the divalent ions investigated here form complexes with the $-COO^-$ group. The strength of complex formation can be expressed by stability constants, $K_1, K_2, \ldots, K_n$, defined as

$$K_1 = \frac{[MA]}{[M][A]} \quad \text{for } M + A \rightleftarrows MA$$

$$K_2 = \frac{[MA_2]}{[MA][A]} \quad \text{for } MA + A \rightleftarrows MA_2$$

$$K_n = \frac{[MA_n]}{[MA_{n-1}][A]} \quad \text{for } MA_{n-1} + A \rightleftarrows MA_n$$

where [M], [A] and [MA] are the concentrations of a divalent ion, the ligand ($-COO^-$) and their complex, MA, respectively. In table 1, we list K_1 values for complex formation between propionate ion and various divalent cations, in comparison with the Raman band shift and other information concerning complex formation in this work. It is found that divalent metal ions with large stability constants, such as Cu^{2+} and Zn^{2+}, show Raman band shifts, whereas Mg^{2+} and Ba^{2+} with small stability constants show none. Therefore, it is reasonable to suppose that bond formation between polymeric $-COO^-$ and Mg^{2+} or Ba^{2+} scarcely occurs. Specific bond formation and purely ionic interaction may be two extreme cases. There must be various stages in the interaction between carboxyl groups and cations. Raman spectroscopy can clearly differentiate specific bond formation from the other but cannot distinguish between various stages of ionic ion binding.

Table 1

Comparison of the Raman frequency shift with the stability constant, K_1

Raman frequency shifts were observed for those cations denoted by +. The potentiometric titration curves in fig. 5 were classified into three groups, A–C. The stability constants were obtained from refs. 21–23.

	Raman band shift		Potentiometric titration curves	Stability constant (pK_1)
	Poly (acrylic acid)	Propionic acid		
Cu^{2+}	+	+	A	2.06–2.3
Mn^{2+}	+	+	B	
Zn^{2+}	+	+	B	1.01–1.08
Ni^{2+}	0	0	B	0.73
Mg^{2+}	0	0	C	0.54
Ba^{2+}	0	0	C	0.15–0.34

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References

1 S.A. Rice and M. Nagasawa, Polyelectrolyte solutions (Academic Press, New York, 1961).
2 S. Koda, H. Nomura and M. Nagasawa, Biophys. Chem. 15 (1982) 65.
3 M. Mandel, J. Polym. Sci. C 16 (1967) 2955.
4 J.C. Leyte, L.H. Zuiderweg and J.J. van der Klink, in: Polyelectrolytes, ed. E. Selegny (D. Reidel, Dordrecht, 1974) p. 383.

5 F.T. Wall and S.J. Gill, J. Phys. Chem. 58 (1954) 1128.
6 H. Morawetz, J. Polym. Sci. 17 (1955) 442.
7 A.M. Kotliar and H. Morawetz, J. Am. Chem. Soc. 77 (1955) 3692.
8 H.P. Gregor, L.B. Luttinger and E.M. Loebl, J. Phys. Chem. 59 (1955) 34.
9 S. Lapanje and S. Oman, Vestn. Slov. Kem. Drust. 12 (1965) 25.
10 M. Mandel and J.C. Leyte, J. Polym. Sci. A 2 (1964) 2883.
11 N. Kono and A. Ikegami, Biopolymers 4 (1966) 823.
12 S.W.T. Westra and J.C. Leyte, J. Magn. Resonance 34 (1979) 475.
13 S.W.T. Westra and J.C. Leyte, Red. J. Roy. Neth. Chem. Soc. 98 (1979) 86.
14 S.W.T. Westra and J.C. Leyte, Ber. Bunseges. Phys. Chem. 83 (1979) 678.
15 P.C. Karenzi, B. Meurer, P. Spegt and G. Weill, Biophys. Chem. 9 (1979) 181.
16 B. Meurer, P. Spegt and G. Weill, Biophys. Chem. 16 (1982) 89.
17 J.C. Leyte, L.H. Zuiderweg and H.J. Vledder, Spectrochim. Acta 23A (1967) 1397.
18 J.C. Leyte, in: Polyelectrolytes, ed. E. Selegny (D. Reidel, Dordrecht, 1974) p. 336.
19 K. Nakamoto, Infrared and Raman spectra of inorganic and coordination compounds, 3rd edn. (John Wiley & Sons, New York, 1978).
20a J. Fujita, A.E. Martell and K. Nakamoto, J. Chem. Phys. 36 (1962) 324; 20b J. Fujita, A.E. Martell and K. Nakamoto, J. Chem. Phys. 36 (1962) 331.
21 M. Lloyd, V. Wycherley and C.B. Monk, J. Chem. Soc. (1951) 1786.
22 R.K. Cannan and A. Kibrick, J. Am. Chem. Soc. 60 (1938) 2314.
23 IUPAC Chemical Data Series 22, Stability constants of metal-ion complexes, part B (organic ligands) (Pergamon Press, New York, 1979).