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THE RELEASE OF MONOVALENT COUNTERIONS BY ADDITION OF DIVALENT COUNTERIONS IN COULOMBIC INTERACTION SYSTEM OF POLYIONS (II)

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In this work, the increase in activity, Δa_+, of a monovalent counterion (Na^+) resulting from the addition of a divalent ion (Cu^{2+}) was experimentally investigated in sulfate or sulfonate polyelectrolyte solutions. It was found that in the case of polyvinylsulfonate, a_+ was expressed by $\Delta a_+ = \Delta(C_{++} - a_{++})$, where C_{++} and a_{++} represent the molar concentration and activity of added Cu^{2+}, respectively; while in the case of dextran sulfate, the expression of Δa_+ became $\Delta a_+ = 2\Delta(C_{++} - a_{++})$. Considering that interactions between these cations and sulfate or sulfonate groups are purely electrostatic, these results were analyzed in relation to the conformation of the polyelectrolytes.

1. Introduction

Fundamental studies on the interaction between a polyion and low molecular weight ions, which is a very important subject in the understanding of various biological functions, have been widely done theoretically and experimentally. In solutions of polyions having only coulombic interactions with their counterions, the establishment of the additivity rule of counterion activity, osmotic pressure or electric conductivity has been examined especially in rod-like polyion solutions [1–4].

In the theories, the additivity rule has been limited to the solutions of a single species of counterion [5–7]. This condition, however, can be extended to systems having multiple species of counterions, both in theory and experiment, provided that the interactions between polyions and low molecular weight ions are electrostatic [4,8].

In a previous paper, we presented a theory based on the Fokker-Planck and Poisson equations and showed that the increase in the activity of monovalent counterions, Δa_+, resulting from the addition of divalent counterions, is expressed by the decrease in activity of the added divalent counterions, $-\Delta a_{++}$ (in molarity units), in the following form:

$$\Delta a_+ = \Delta C_{++} - \Delta a_{++} \qquad (1)$$

where C_{++} represents the molar concentration of added divalent counterions [8]. In the case of covalent binding of divalent counterions to a polyion, Δa_+ is thought to be given by $2\Delta(C_{++} - a_{++})$ from the simple consideration that a divalent counterion masks a monovalent ionized group on the polyion with its double charge repelling the bound monovalent counterions. Recently, a result similar to that of eq. (1) for the osmotic coefficient in relation to the activities of multiple species of counterions has been reported by Vlachy and Bratko [9]. Since eq. (1) is derived under the assumption of a thin rod-like conformation of polyions besides the coulombic interaction, some revision is necessary when one applies this equation to a more realistic system.

In this paper, in order to check the validity of eq. (1), we chose sodium polyvinylsulfonate or sodium dextran sulfate as polyelectrolytes, and $CuSO_4$ as the divalent salt added, considering that Cu^{2+} is thought to be not covalently bound to these sulfate or sulfonate polyions and its activity is precisely measurable with a Cu^{2+}-sensitive solid membrane electrode [10].

2. Experimental

2.1. Materials

Sodium dextran sulfate ($\overline{M}_w = 50000$, S content = 19.2%) was supplied by Meitoh Sangyo Co., Ltd. Its purification and standardization were performed in the following way.

Firstly, 1.0 g of sodium dextran was completely dissolved in 50 ml redistilled water and dialyzed against deionized redistilled water at 5°C to remove excess low molecular weight salts and contaminations from the polymer.

Sodium dextran was then converted completely to the acid form by exchanging the counterions from Na^+ to H^+ with Dowex-50 resin. Removal of the main impurities and concentration of the solutions were simultaneously carried out by diafiltration in a 65 ml stirred ultrafiltration cell (52 Amicon Corp., Lexington, MA) with a diaflow membrane (UM; molecular weight cut-off of 10000) under nitrogen gas. Standardization of dextran sulfate was performed immediately after the concentration by titration against a standard NaOH solution.

The potassium salt of polyvinylsulfonate was purchased from Nakarai Kagaku Co., Ltd. The procedures of purification, conversion to the acid form and standardization were performed in the same way as described above.

All the aqueous solvents used were distilled, deionized by ion exchange and redistilled till the electric resistance was more than 500 kΩ/cm with a pyrex glass apparatus. NaOH solution for the standardization and potentiometric investigation was prepared by dilution of a saturated NaOH solution with CO_2-free redistilled water, the standardization being made by titration with standard HCl.

2.2. Measurements

Conductivity measurements were performed with the same method as described in the previous paper [11], and the simultaneous activity measurements of Na^+ and Cu^{2+} were carried out in the same way as described in ref. [8].

3. Results and discussion

In fig. 1, the increase in activity of the released Na^+ and that of the inactive Cu^{2+}, $C_{Cu^{2+}} - a_{Cu^{2+}}$ (on a molar scale) are plotted against the added $CuSO_4$ concentration (on a molar scale) for the case of the sodium salt of dextran sulfate at $C_p =$ 0.01 and 0.001 N. Obviously, this result shows that the two Na^+ originally captured by electrostatic interaction in the polyion domain are replaced by the one added Cu^{2+} in the added Cu^{2+} concentration range ($C_{Cu^{2+}} \leqslant C_p$).

Similar results have also been observed in systems in which specific binding is formed between a polyion and counterions, for example, in systems of carboxylic polymers and some divalent cations [8].

On the other hand, the differences between the specific conductivity of sodium dextran sulfate, K_p, and that of the low molecular weight salt solution, K_s, when adding a simple salt are shown in fig. 2. As seen in this figure, $K_p - K_s$ is almost independent of the added low molecular weight salts in the case of Na^+ and Cu^{2+} counterions. These results demonstrate that only electrostatic binding is formed between the polyion and these counterions, while in the case of the Ba^{2+} counterion, covalent binding formation seems to take place.

In table 1, the increasing rate of released Na^+ activity per added Cu^{2+} (A), and that of the inactivity of Cu^{2+} (B), are shown for various polyion concentrations at each initial stage (upper column) and at the final stage (lower column) of Ca^{2+} addition. Clearly, in the case of sodium dextran, the value of A/B is nearly equal to 2.0 in the initial stage. This result is contradictory to the relationship of eq. (1), in other words, in the case of dextran sulfate the thin rod-like model is not applicable. This is naturally deduced from the following experimental and theoretical facts. (1) Analysis of the relationship between the intrinsic viscosity $[\eta]$ and the molecular weight M_n for the higher molecular weight ($M_n > 2000$) sodium dextran in water shows that the value of the exponent a in the Mark-Houwink-Sakurada relationship $[\eta] = K \cdot M_n^a$ lies between 0.5 and 0.6, viz., sodium dextran has a random-coil conformation

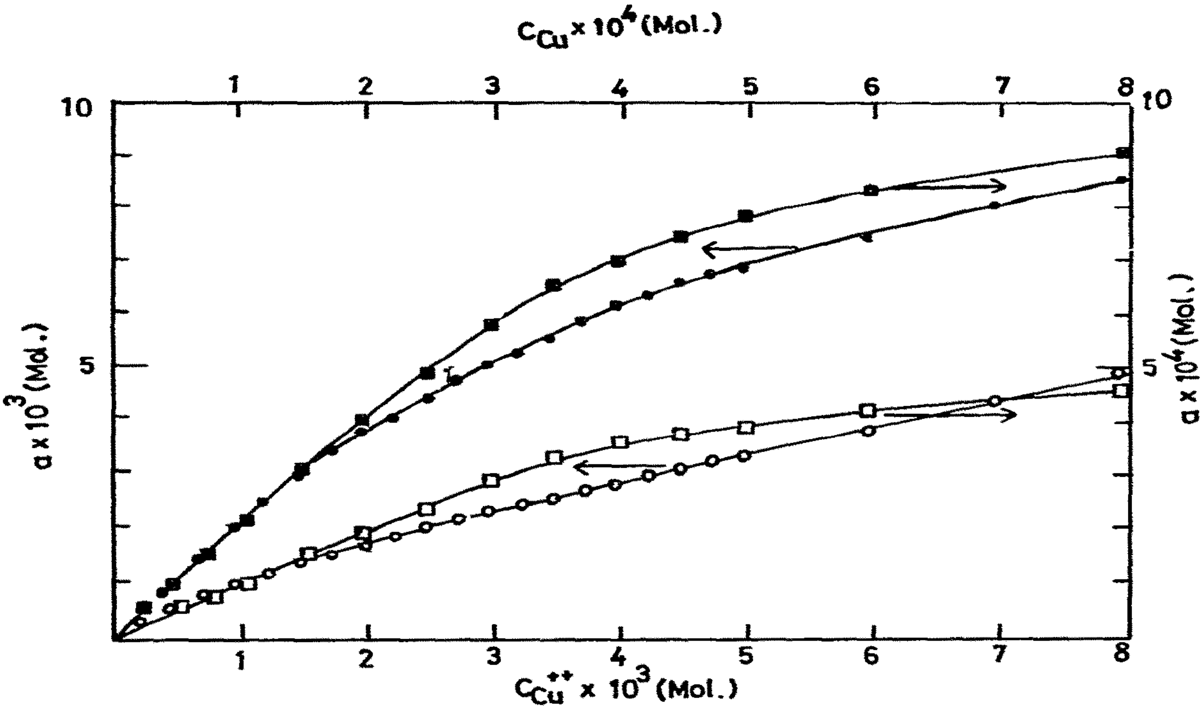

Fig. 1. Plot of the activity increase of Na^{-}, Δa_{Na^+}, and that of the inactive Cu^{2-}, $C_{Cu^{2+}} - a_{Cu^{2+}}$ (on a molar scale) versus added $CuSO_4$ (molar scale) at constant sodium dextran concentrations at 25°C. ■, Δa_{Na^+}; □, $C_{Cu^{2+}} - a_{Cu^{2+}}$ at $C_p = 0.001$ N (upper and right-hand scale) and ●, Δa_{Na^+}; ○, $C_{Cu^{2+}} - a_{Cu^{2+}}$ at $C_p = 0.01$ N (lower and left-hand scale).

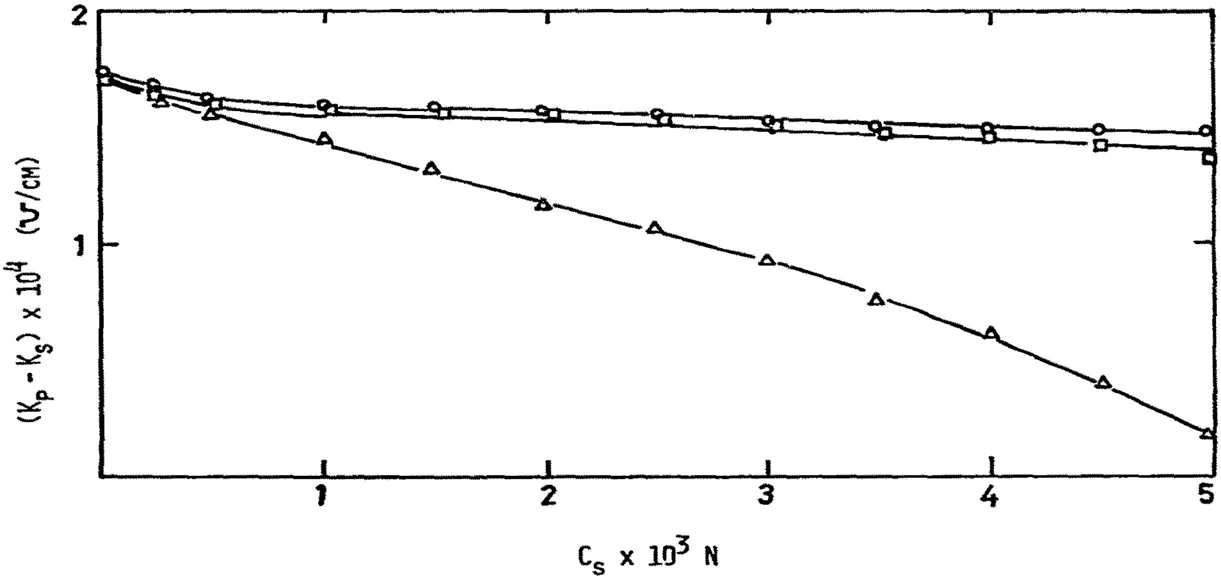

Fig. 2. The increment of specific conductivity $K_p - K_s$ ($\Omega^{-1} \cdot cm^{-1}$) of dextran solution $C_p = 0.01$ N) against added salt concentration (on a normal scale). ○, NaCl; □, $CuSO_4$; and △, $BaCl_2$.

Table 1

The values of $A=\Delta a_{Na^+}/\Delta C_{++}$ and $B=\Delta(C_{++}-a_{++})/\Delta C_{++}$ at constant polyion concentration

The upper row shows the values at the initial stage ($C_s < \frac{1}{4}C_p$) and the lower row those of the final stage ($C_s \doteqdot C_p$). The values of polystyrenesulfonate are taken from ref. [8].

Sodium salt	C_p (N)	$A=\dfrac{\Delta a_+}{\Delta C_{++}}$	$B=\dfrac{\Delta(C_{++}-a_{++})}{\Delta C_{++}}$	A/B
Polyvinylsulfonate	0.01	1.17	0.96	1.22
		0.068	0.145	0.47
	0.005	1.29	0.97	1.33
		0.38	0.55	0.69
	0.001	1.33	0.98	1.36
		0.58	0.44	1.32
Dextran sulfate	0.01	1.92	0.95	2.02
		0.48	0.52	0.93
	0.005	2.17	1.00	2.17
		0.52	0.42	1.24
	0.001	1.96	0.94	2.09
		0.53	0.30	1.77
Polystyrenesulfonate	0.002	1.60	0.9	1.67
		0.43	0.53	0.91

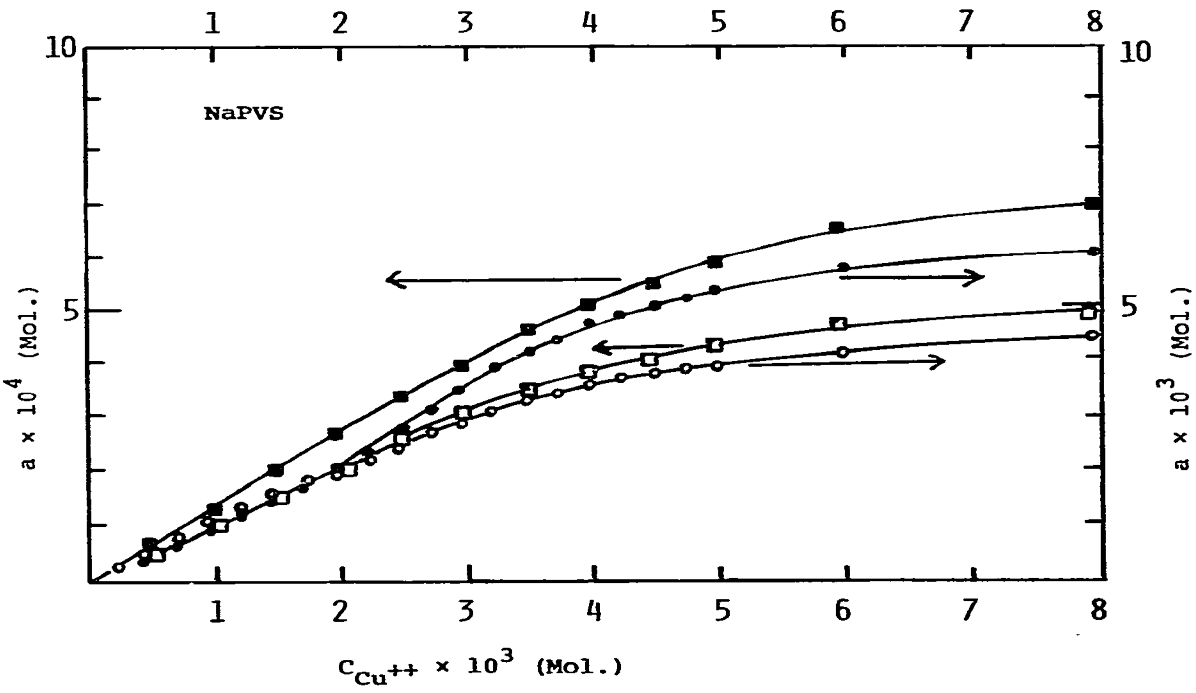

Fig. 3. The activity increase of Na$^-$, Δa_{Na^+}, and the inactive Cu^{2+}, $C_{Cu^{2+}}-a_{Cu^{2+}}$ (on a molar scale) against added CuSO$_4$ (molar scale) at constant polyvinylsulfonate concentrations at 25°C. ■, Δa_{Na^+}: □, $C_{Cu^{2+}}-a_{Cu^{2+}}$ at $C_p=0.001$ N (upper and left-hand scale) and ●, Δa_{Na^+}: ○, $C_{Cu^{2+}}-a_{Cu^{2+}}$ at $C_p=0.001$ N (lower and right-hand scale).

[13–15]. (2) Taking into consideration the fact that dextran has a molecular structure consisting of an α(1-6) bond between D-glucose monomers, it should have a extended rod-like conformation, however, in reality it has a random-coil conformation [16]. This suggests that the overall structure of dextran sulfate never has a thin rod-like conformation. (3) Dextran, more or less, has a branching structure such as (1 → 2), (1 → 3) and (1 → 4) bonds. Generally, the existence of branching, even if only slight, makes the polymer structure very entangled.

On the other hand, in a relatively high Cu^{2+} concentration range, the value of A/B is nearly 1.0, suggesting that the polyion takes on a rigid rod-like conformation [17].

In fig. 3, the increase in Na^+ activity and that of inactivated Cu^{2+} (on a molar scale) are indicated for the sodium salt of polyvinylsulfonate as a function of the added $CuSO_4$ concentration at $C_p = 0.01$ and 0.001 N.

Evidently, these results support the approximate establishment of the theoretical relationship, eq. (1), i.e., one Na^+ originally electrostatically bound in the polyion domain is replaced by one added Cu^{2+}. On the other hand, the values of $K_p - K_s$ of sodium polyvinylsulfonate are shown as a function of the added salt concentration in fig. 4. From this figure it turns out that, as in the

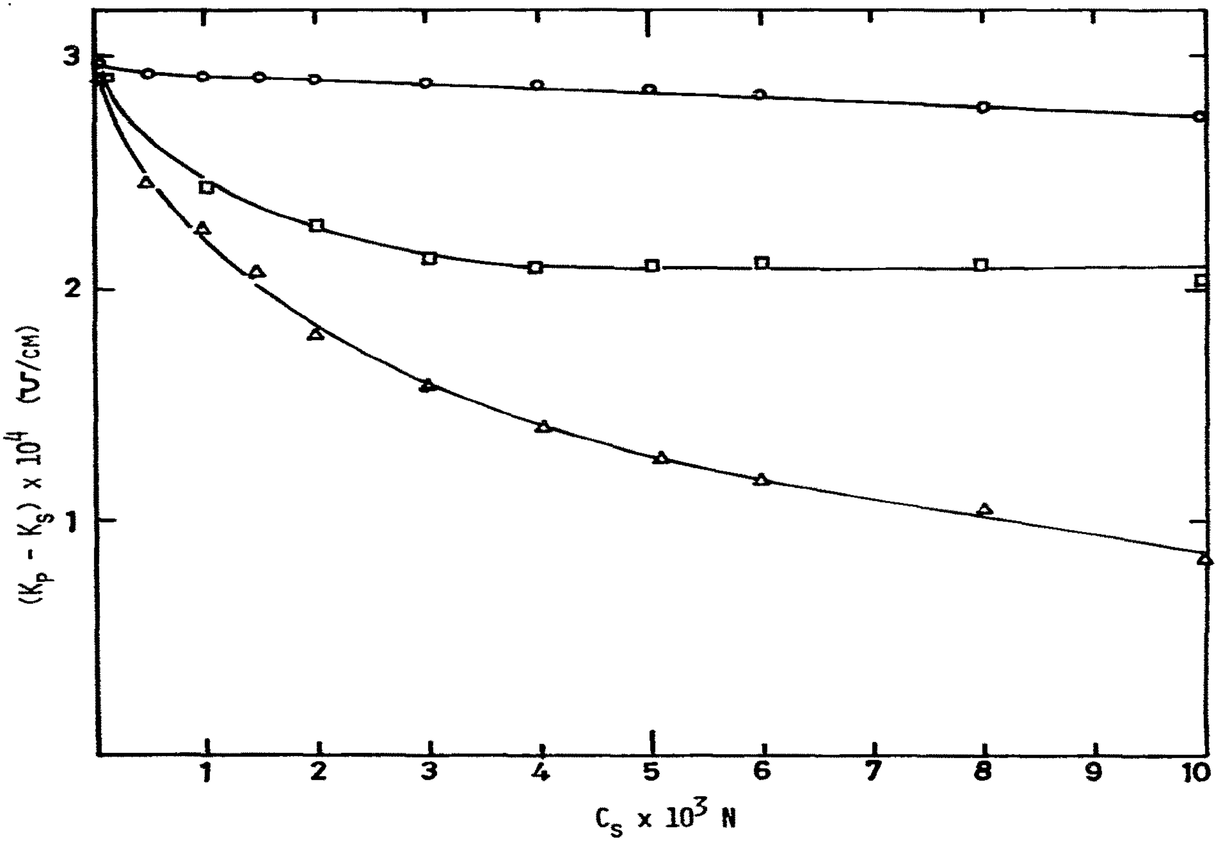

Fig. 4. The increment of specific conductivity $K_p - K_s$ ($\Omega^{-1} \cdot cm^{-1}$) of polyvinylsulfonate solution ($C_p = 0.005$ N) against added salt concentration (on a normal scale). ○, NaCl; □, $CuSO_4$; and △, $BaCl_2$.

case of dextran, Ba^{2+} counterions form tight specific covalent bonds, while Cu^{2+} or Na^{+} counterions never make such a covalent formation. As shown in table 1, in the case of polyvinylsulfonate, the value of A/B is about 1.0 in the low added Cu^{2+} concentration range, and even for a higher Cu^{2+} concentration range ($C_s \doteqdot C_p$) the A/B value is less than 1.00.

This fact is consistent with the result that the potentiometric titration behavior is well explained by the use of the thin rigid rod-like model [18].

Generally, eq. (1) may be established experimentally and theoretically for a polyion having a thin rod-like conformation which has a purely electrostatic interaction with counterions.

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