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THE RELEASE OF MONOVALENT COUNTERIONS BY ADDITION OF DIVALENT COUNTERIONS IN COULOMBIC INTERACTION SYSTEM

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The additivity rule of counterion activity or osmotic pressure in rodlike polyelectrolyte solutions has been discussed on the basis of the Fokker–Planck and Poisson equations in relation to the fluctuation of counterion distribution. This new theory has concluded that the additivity rule of counterion activity is less applicable than that of osmotic pressure due to the electric expansion force acting on the free-volume surface resulting from the fluctuation of counterion distribution. The theory has introduced an approximate relation between the counterion activities in the mixture solution of divalent and monovalent counterions, such that $\Delta a_+ = \Delta C_{++} - \Delta a_{++}$, in which Δa_+ represents the increase of activity of monovalent counter-ions resulting from the addition of divalent counterions ΔC_{++} (in molar) to the solution, and Δa_{++} means the increase of the divalent counterion activity (in molar) in this process. This relation has been experimentally examined for Na-PSS solutions in the process of Cu^{2+} ion addition by the use of Na^+ and Cu^{2+} sensitive electrodes, and it has been turned out that the relation is established in the low charge state of polyion.

1. Introduction

The additivity rule of osmotic pressure or counterion activity, which is one of the most important properties of polyelectrolytes solutions, has been theoretically proved mainly for the case of rodlike polyion on the basis of the clustor integral theory or the two dimensional Poisson--Boltzmann equation [1–6].

Usually, the additivity rule has been limited to the solutions of a single species of counterion. It should be noted, however, that these theories can be extended to the system of multi-species of counterions, provided that the interactions between polyions and low molecular ions are electrostatic [7]. It is of interest to examine the theoretical result for the competitive electrostatic binding of different species of counterions to the polyion in their coexisting solutions.

In this paper, at first we will present a new theory describing the additivity rule and general relation between the activities of counterions of various species in the two dimensional rodlike polyion solutions, not based on the Poisson–Boltzmann equation but based on the Fokker–Planck and the Poisson equations. This theory discusses the establishment of the additivity rule in relation to the fluctuation of counterion distribution or neutrality of polyion free-volume. From this theory it is concluded that the additivity rule of osmotic pressure is established for the system of very thin and long rodlike polyions even in the presence of the neutrality fluctuations of the polyion free-volume, while the additivity of counterion activity becomes less available due to the occurrence of the electric expansion force acting on the free volume-surface resulting from the neutrality fluctuation.

Secondary, we will examine whether or not the relation predicted by the theories can be established in the coexistent solution of monovalent and divalent counterions.

The simplest way to perform this examination is to observe the increase of the activity of monovalent counterions resulting from the addition of divalent counterions and to compare the result with the theory. According to the theory, as seen in the next section, the increase of the activity of monovalent counterions, Δa_+, resulting from the addition of divalent counterions, is expressed with the decrease of the activity of added divalent counterions in molarity units, $-\Delta a_{++}$, in the following form;

$$\Delta a_+ = \Delta C_{++} - \Delta a_{++} ,$$

where C_{++} exhibits the molar concentration of added divalent counterion.

This relation is established for the systems of very thin and rodlike polyions where only the electrostatic interactions are involved between the polyion and the counterions. This implies briefly that the amount of the release of the bound monovalent counterions on addition of divalent counterions is equal to the amount of the bound divalent counterions. In the case of covalent binding of divalent counterions to the polyion, Δa_+ must have been given by $2\Delta(C_{++} - a_{++})$, since the divalent counterions mask the polyion with double charges. Therefore, in order to check this relation, it is required in the experiments that both kind of counterions, monovalent and divalent, must not be bound to polyion forming chemical bonds. In this respect, we chose the sodium salt of polystyrene sulfonate (Na-PSS) as a polyelectrolyte and copper sulphate ($CuSO_4$) as an adding divalent salt, since copper ion is thought not to be bound to PSS by non electrostatic interaction. This polyion has been ascertained to take a rodlike conformation, and is suited for the examination of the theoretical results based on the rodlike model [8,9]. Also this system has the merit that the copperion activity can be simply obtained with high accuracy by the use of a reliable copper ion-sensitive solid membrane electrode [10].

Our experimental results showed that the above relation is approximately established in our ($PSS\text{-}Na^+$, Cu^{++}) system over a certain added Cu^{++} ion concentration range.

2. Theory

Let us assume that a rodlike polyion, with radius a and linear charge density ne_0 (assumed to be positive) is situated in the center of its coaxial free-volume of radius R. (see fig. 1). If the averaged velocity of the distributed low molecular ions of species i around the polyion is denoted by $\mathbf{v}_i$, the number concentration of the ith ions, f_i, satisfies the following equation of continuity at time t;

$$\partial f/\partial t = -\nabla \cdot f_i \mathbf{v}_i \, . \tag{1}$$

The reduced electric potential ϕ (defined as the electric potential divided by the Boltzmann factor kT and multiplied by the elementary charge e_0) is described with the cylinder coordinates r, θ, whose origin is at the center of the polyion rod axis, by the Poisson equation;

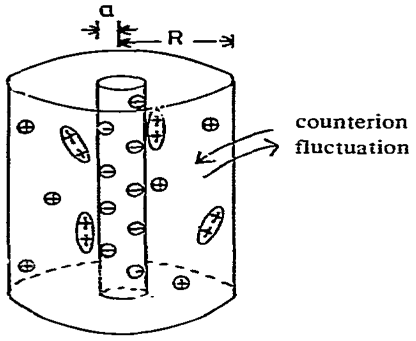

Fig. 1. Model of a rod-like polyion and free volume.

$$\nabla^2\phi = \frac{1}{r}\frac{\partial}{\partial r}(r\phi_r) + \frac{1}{r^2}\frac{\partial}{\partial\theta}\phi_\theta = -4\pi\beta \sum f_i z_i \, , \tag{2}$$

where ϕ_r, ϕ_θ are defined by

$$\phi_r \equiv \partial\phi/\partial r \, , \qquad \phi_\theta \equiv \partial\phi/\partial\theta \, ,$$

and β is defined, with the dielectric constant of solvent denoted by D by

$$\beta = e_0^2/DkT \, .$$

If the ith low molecular ions have a hydrodynamic friction constant ξ_i and valence z_i, the following force-balance equation for a single ith ion is established,

$$-\xi_i \mathbf{v}_i - kT(\nabla z_i \phi + \nabla \ln f_i) = 0 \, . \tag{3}$$

Eq. (1) is transformed into

$$\sum \partial(\xi_i f_i r^2)/\partial t = -\sum (\boldsymbol{\upsilon}\, \xi_i f_i r^2 \mathbf{v}_i) + 2 \sum \xi_i f_i \boldsymbol{r} \cdot \mathbf{v}_i \, ,$$

where Σ denotes the summation over all species of i.

Substitution of eq. (3) into the above relation leads to the following equation in the integral form, under consideration of eq. (2) for the $\Sigma f_i z_i$ term;

$$\sum \int^V \frac{\partial \xi_i f_i r^2}{\partial t} \mathrm{d}V = -\sum \int^V \nabla \cdot \xi_i f_i r^2 \mathbf{v}_i \mathrm{d}V$$
$$- 2kT \sum \int^V \boldsymbol{r} \cdot \nabla f_i \mathrm{d}V + 2kT \int^V (\nabla^2\phi/4\pi\beta) \boldsymbol{r} \cdot \nabla \phi \mathrm{d}V, \tag{4}$$

where the integration is to be performed over the whole free-volume V. It is important that each of the integration terms on the right-hand side of eq. (4) can be transformed into the surface integrals on the polyion and the free-volume by the Gauss theorem.

The first term is expressed by the ion-fluxes passing through the polyion surface and the free-volume surface in the perpendicular direction, such that,

$$\int^{V} \mathbf{\nabla}\cdot f_i r^2 \mathbf{v}_i \,\mathrm{d}V = \int^{S_R} f_i v_{in} R^2 \mathrm{d}S_R - \int^{S_a} f_i v_{in} a^2 \mathrm{d}S_a \,,$$

where S_R and S_a represent the surfaces on the free-volume $(r = R)$ and on the polyion rod $(r = a)$, respectively, and V_{in} and $f_i v_{in}$ are ion velocity and ion flux in the direction perpendicular to the corresponding surfaces, respectively.

Let us take the time-average on these ion-fluxes. Considering the physical condition that the time-average of the ion-fluxes through the surfaces S_R and S_a should vanish in the fluctuation process of low molecular ions, we have

$$\left\langle \int^{V} \mathbf{\nabla}\cdot f_i r^2 \mathbf{v}_i \,\mathrm{d}V \right\rangle_t = 0 \,, \tag{5}$$

where $\langle\ \rangle_t$ represents the time average.

The second term on the right-hand side of eq. (4) can be transformed into the following form without difficulty;

$$\int^{V} \boldsymbol{r}\cdot\mathbf{\nabla} f_i \,\mathrm{d}V = 2\pi\,\{R^2 f_i(R) - a^2 f_i(a)\} - 2VC_i \,, \tag{6}$$

where C_i is the spacial average concentration of ith ions in V. The time average on the both sides of eq. (6) is simply given by replacing $f_i(R), f_i(a)$ and C_i in eq. (6) with $\langle f_i(R)\rangle$, $\langle f_i(a)\rangle$ and $\langle C_i\rangle$, respectively. The third term on the right hand side of eq. (4) can be transformed into the following form by the use of the Gauss theorem;

$$\frac{kT}{2\pi\beta}\int^{V} \nabla^2\phi\, \boldsymbol{r}\cdot\mathbf{\nabla}\phi \,\mathrm{d}V = 4\pi R^2 X$$
$$-\frac{kT}{4\pi\beta}\int_0^{2\pi} \{a^2\phi_r^2(a,\theta) - \phi_\theta^2(a,\theta)\}\,\mathrm{d}\theta \,, \tag{7}$$

where ϕ_r and ϕ_θ represent $\partial\phi/\partial r$ and $\partial\phi/\partial\theta$, respectively, and X, defined by the following relation, denotes the electric expansion force per unit area on the free-volume surface.

$$X = \frac{D}{8\pi}\frac{1}{2\pi R}\int_{C}^{2\pi} \left(\frac{kT}{e_0}\right)^2 \left(\phi_r^2 - \frac{\phi_\theta^2}{R^2}\right)_{r=R} R\,\mathrm{d}\theta \,. \tag{8}$$

It is important that the time-average of ϕ_r, that is $\langle\phi_r\rangle$, must be zero on the free-volume surface because of the neutrality of the free-volume and of course $\langle\phi_\theta\rangle = 0$, but $\langle\phi_r^2\rangle$ or $\langle\phi_\theta^2\rangle$ remains finite in the process of the fluctuation of counterion distribution. Thus, the electric expansion force X may appear on the free-volume surface causing a negative pressure on the system.

The term on the left-hand side of eq. (4) vanishes on taking the time-average of this term, since in the fluctuation process the relation

$$\langle \partial f_i/\partial t\rangle_t = 0 \,, \tag{9}$$

should be established anywhere in the free-volume.

If the polyion radius a is assumed to be infinitely small, that is if $a/R \to 0$, we can assume that the quantities $a^2 f_i(a)$ in eq. (6) and $\phi_\theta(a)$ in eq. (7) may be put to be zero. The value of $a\phi_r(a)$ in eq. (7) can be expressed by linear number density of polyion charge, n, as:

$$a\phi_r(a) = -n\beta \,.$$

Thus, the following final relation is obtained from eq. (4).

$$kT\left(-\sum\langle C_i\rangle + \sum\langle f_i(R)\rangle\right) - X = \tfrac{1}{2} n\lambda/V \,, \tag{10}$$

where $\lambda\ (\equiv n\beta)$ is the well known charge parameter. The time-average of overall concentration of ith ion, $\langle C_i\rangle$, is simply written by the usual concentration C_i and the average concentration on the free-volume surface, $f_i(R)$, can be regarded as the activity of ith ion, a_i, so that the above equation is written as

$$kT\sum a_i - X = kT\sum C_i - \tfrac{1}{2} n\lambda/V \,. \tag{11}$$

The term on the left-hand side of eq. (11) represents the pressure on the free-volume surface which is measured as the osmotic pressure of the solution Π.

Especially for the solutions of monovalent positive counterions and monovalent negative byions, since ΣC_i is $\Sigma C_i = C_s + (n/V)$, eq. (11) becomes

$$\Pi = \Pi_0 + kT(n/V)(1 - \tfrac{1}{2}\lambda) \,, \quad (\Pi_0 \equiv 2C_s kT) \,, \tag{12}$$

where Π_0 is a contribution of osmotic pressure by added salt. This relation is valid for $\lambda \leqslant 1$ and in the case $\lambda > 1$, Π stays constant at $\lambda = 1$ according to the ion-condensation theory in which $a^2 f_i(a)$ term in eq. (6) is still fixed at zero as a tends to zero.

Thus, for the osmotic pressure, the additivity rule is established. It is important that the additivity of counterion activity, however cannot be obtained unless the term X can be ignored. It is supposed that in the absence of salt or in the case of dilute salt solutions, X may be neglected. Since the concentration of the byion may be regarded as the activity, one can put $C_- = a_-$, and eq. (11) leads to the approximate relation available when $X=0$ for the system of multicomponents of counterion species:

$$\sum a_i = \frac{n}{V}(1 - \tfrac{1}{2}\lambda) + \sum C_i \,. \tag{13}$$

Let us treat the case when divalent salt is added to the polyion solution having originally only monovalent counterions. From eq. (13), the increase of the activity of monovalent counterions, due to the addition of ΔC_{++} of divalent counterion, Δa_+, is expressed by

$$\Delta a_+ / \Delta C_{++} = \Delta(C_{++} - a_{++}) / \Delta C_{++} \,, \tag{14}$$

under the approximation that the activity of byions a_- is nearly equal to be the concentration of byions C_-. In the eq. (14) $\Delta(C_{++} - a_{++})$ represents the amount of bound divalent counterions on the addition of the divalent counterions. This rule implies that one bound divalent counterion releases one monovalent, gradually masking the polyion charge on the successive addition of divalent salts. It is of interest to check this equation experimentally and this is the purpose of our present study.

3. Experimental section

3.1. Materials

The sodium salt of poly(styrenesulfonate) (NaPSS) (average mol wt 5×10^4) was supplied by the courtesy of Dr. I. Noda. Purification and standardization of the sample were carried out in the following way.

At first 1.0 g of NaPSS was perfectly dissolved in pure water of 50 ml and dialysed against deionized redistilled water at 5°C for 3 days to remove excess simple salt and contamination of low molecular weight fragments. NaPSS was then converted completely to the acid form by exchanging Na^+-counterions to H^+-ions with Dowex-50 resin. Removal of the main impurities and concentration of the solution were carried out by diafiltration in a 65 ml stirred-ultrafiltration cell (52 Amicon Corp., Lexington, Mass.) using a diaflow membrane (uM. 10; molecular weight cut-off of 10 000) under nitrogen gas. Standardization of HPSS was then performed by titration against standard NaOH, and the neutralized PSS (NaPSS) was stocked at 5°C.

An alternating copolymer of ethylene and maleic anhydride was purchased from Scientific Polymer Products, Inc. (New York). The procedures of purification, conversion to acid-form and standardization of the final stock solutions were described earlier [11], and removal of the impurities was carried out in the same way as described above. All the aqueous solvents used were distilled, deionized by ion exchange and redistilled with pyrex-glass apparatus till each electric resistance exceeded 500 kΩ/cm.

The sodium hydroxide used for the standardizations and the potentiometric investigations was prepared by dilution of a saturated NaOH solution with almost CO_2-free redistilled water, and its standardization was made by the titration with a standard HCl. Used salts, NaCl, $CuSO_4$ and Na_2SO_4 were ultrapure or of special reagent grade, and they were used without further purification.

3.2. Measurements

3.2.1. Conductivity measurements

The conductivity measurements were performed by the same method as described in the previous paper [11].

3.2.2. Activity measurements

For the simultaneous measurements of Na^+ ion and Cu^{2+} ion activities, both a Na^+-ion selective glass electrode (CE 1200, Toko Kagaku Co. Ltd., Tokyo) and a Cu^{2+} ion selective solid membrane electrode (no. 94–29, Orion Research, Inc., Cambridge) were inserted into a 20.0 ml aqueous solution of NaPSS at a fixed concentration in a glass cell immersed in an isothermal water bath at 25 ± 0.01°C under nitrogen gas. A saturated calomel reference electrode is prepared in a separate vessel in the same bath whose saturated KCl

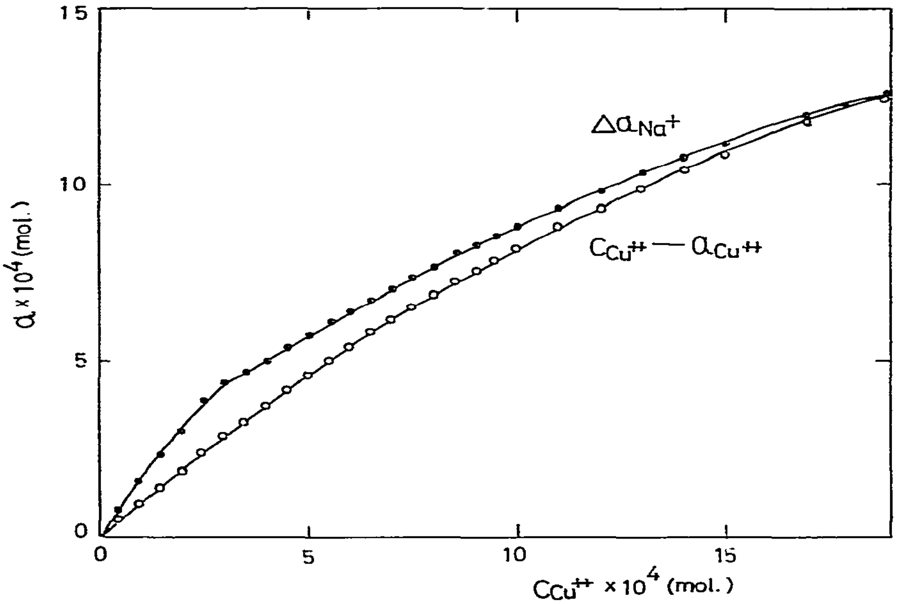

Fig. 2. The activity increment Δa_{Na^+} of Na^+ ion and the inactive Cu^{2+} ion ($C_{\mathrm{Cu}^{2+}} - a_{\mathrm{Cu}^{2+}}$) versus added $\mathrm{CuSO_4}$ (molarity) at constant PSS concentration (0.002 mol.) at 25°C; —●—: Δa_{Na^+}(mol.), —○—: $C_{\mathrm{Cu}^{2+}} - a_{\mathrm{Cu}^{2+}}$(mol.).

solution is connected to the cell through a KCl liquid junction tube with a pin-hole at its end. The pin-hole is made so that the leakage of KCl into the solution is as small as possible within the error of the liquid junction potential.

The reliability of the Cu^{2+}-ion selective electrode and its complementary apparatus was assured by the plots of the potential versus the logarithm of the Cu^{2+} ion concentration in polyion-free 0.5 M $\mathrm{Na_2SO_4}$ solutions as described in ref. [12]. It was concluded that our Cu^{2+} ion sensitive electrode was available in Cu^{2+} concentration range over 10^{-5} N. Calibration of the electrode system was made before and after each experiment. The reliability of the Na^+-ion selective electrode was assured by the plot of the potential versus the logarithm of the Na^+ ion activity (quoted from the tables [13]) in polyion-free solutions which formed always a straight line with the expected nernstian slope (59.2 mV per ten-fold Na^+-ion activity change) in the concentration region over 5×10^{-4} N.

For the accurate addition of small amount of $\mathrm{CuSO_4}$ to the cell, a 0.5 ml ultra precision microburet (Metrohm E-457) with the finest scale division 0.5 μl was employed. Equilibriation of the solutions after each addition of titrant was made by the method described elsewhere [10]. Since there is a light effect on the standard potential of the Cu^{2+}-ion selective electrode (2 to 5 mV), the whole apparatus was covered with a steel box to avoid the light, which was also effective for electric shielding. The potential readings of both electrodes, detected by a Hitachi-Horiba and a Yokogawa ionmeter with the help of a connected two-pen recorder, achieved the desired precision within an error of 0.02 mV.

4. Results

In fig. 2, the increment of Na^+ ion activity (Δa_{Na}) and the inactive molar Cu^{2+} ion concentration, $C_{\mathrm{Cu}} - a_{\mathrm{Cu}}$, are plotted against the added $\mathrm{CuSO_4}$ molar concentration C_{Cu}. As seen in this figure, the amount of Δa_{Na} is almost the same as the amount of ($C_{\mathrm{Cu}} - a_{\mathrm{Cu}}$) when C_{Cu} exceeds nearly 0.3 mN. This result concludes that the theoretical relation, eq. (14), is almost perfectly established experimentally, provided that C_{Cu} is rather high. In the case C_{Cu} is smaller than 0.3 mN, Δa_{Na} becomes nearly two times larger than the

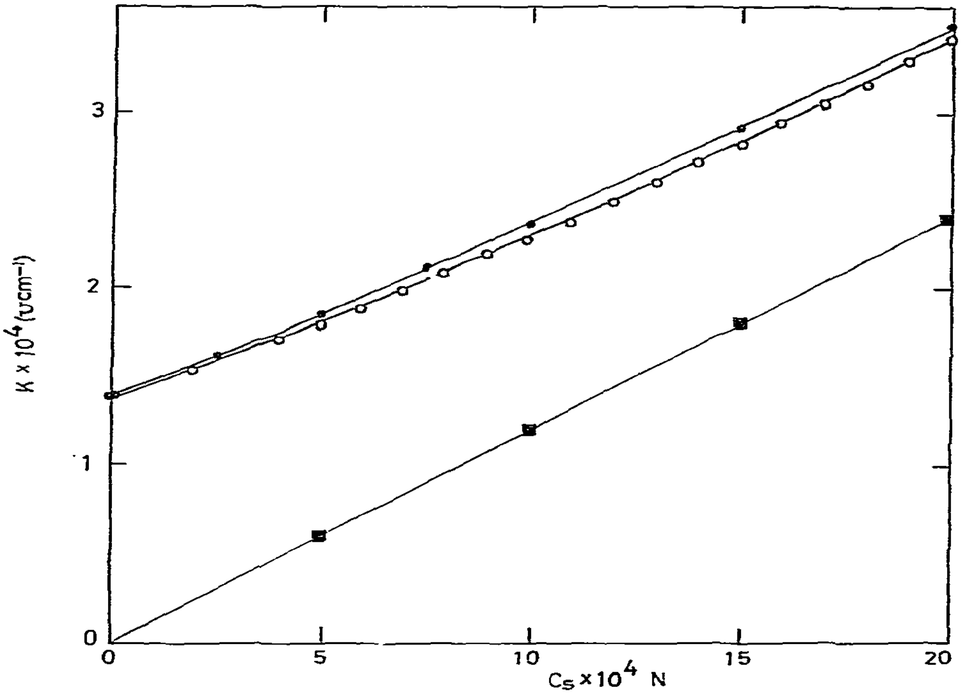

Fig. 3. The specific conductivities K (mho cm^{-1}) of NaPSS versus the concentration of the added $CuSO_4$ at constant polyion concentration ($C_p = 0.004$ mono mol.) at 25°C; —●—: the experimental specific conductivities, —○—: the calculated specific conductivities, and —■—: the specific conductivities of the simple $CuSO_4$ solution.

bound Cu^{2+} concentration, $C_{Cu} - a_{Cu}$. This implies that when the added Cu^{2+} concentration is lower than about 1/10 of monomer concentration, eq. (14) becomes invalid, and instead one Cu^{2+} ion binding becomes to correspond to two released Na^+ counterions like the case of covalent Cu^{2+} ion-formation with the polyion.

The above theory is established only for the system of electrostatic interactions. To examine that our PSS-Cu system is mainly of such a electrostatic interaction, the following conductivity measurements were performed. In fig. 3, the specific conductivity, κ, of PSS-Na solutions when adding $CuSO_4$ are shown together with the specific conductivity of simple $CuSO_4$ solutions and the calculated conductivity of polyion solution which was obtained from the values of Cu^{2+} ion and Na^+ ion activities experimentally obtained in the present solutions and the table values of the limiting equivalent conductivity of these ions [14].

As seen in fig. 3, the conductivity line for PSS-$CuSO_4$ solutions is experimentally almost parallel to that for simple $CuSO_4$. A little deviation from the complete parallel can be attributed to the difference of equivalent conductivities between free Na^+ ion and free Cu^{2+} ion. In fact, the coincidence of the experimental line with the line calculated on the basis of the table values of specific conductivities of free Cu^{2+} and Na^+ ions is satisfactory in fig. 3. A completely different feature of the conductivity is observed in the case of strong Cu^{2+} ion-binding forming a Cu^{2+} ion chelation between the two neighbouring ionized carboxyl groups, for instance in poly (Et-CO-MA) solutions as a typical case, the result of which is shown in fig. 4.

5. Discussions

The coincidence of the experimental result with eq. (14) is satisfactory at least as a first approximation.

It should be remarked that our theoretical results of

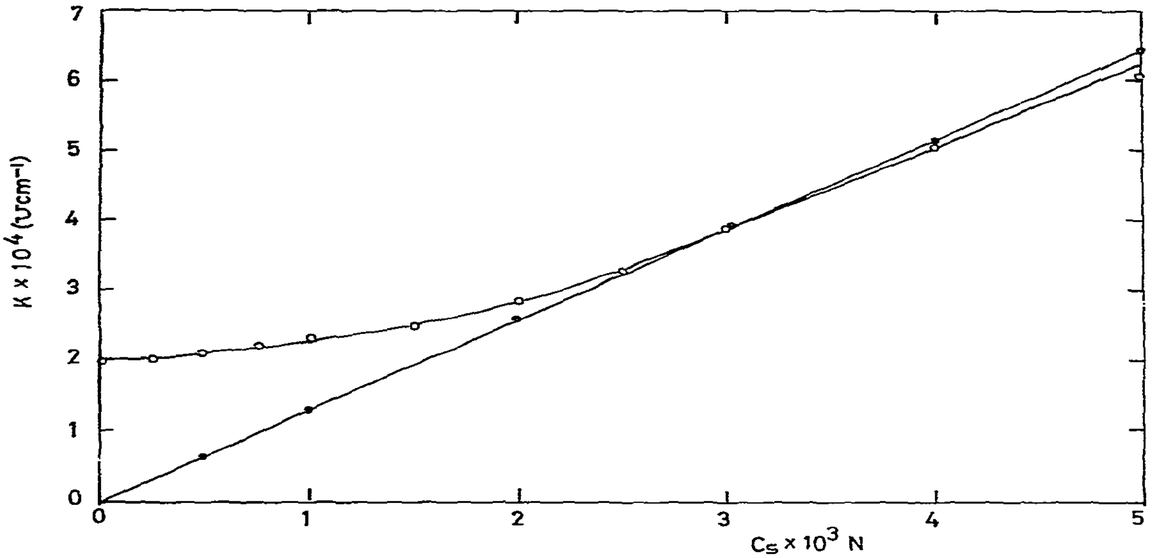

Fig. 4. The specific conductivities K (mho cm^{-1}) of sodium salt of poly(Et-co-MA) versus the concentration of the added $CuSO_4$, at the constant polyion concentration (C_p = 0.004 mono mol.) at 25°C; —○—: the specific conductivities of Cu^{2+}–Na_p(Et-co-MA) systems, —●—: the specific conductivities of simple $CuSO_4$ solution.

eqs. (11), (13) and (14), have been based on the assumptions of, (1) the absence of non-coulombic interaction, (2) the two dimensional polyion system (namely rod-like polyion solution) and (3) the neglect of the $a^2 f_i(a)$ term in eq. (6) as a limiting case of a/R tending to zero.

In the case of high charge-density, the term $a^2 f_i(a)$ cannot be neglected, because of the high values of $f_i(a)$ when a tends to zero. If the value of $a^2 f_i(a)$ is kept constant against the charge increase, as expected from the ion-condensation theory, eq. (14) can similarly be established. However, in the case of the two mixed species of counterions, there is no guarantee of a constant $a^2 f_i(a)$ value against the mixing ratio. In fact, as seen in our experiments, the value of $\Delta a_{Na}/(C_{Cu} - a_{Cu})$ exceeds unity by nearly 2.0. This is supposed to be due to the non-zero or not constant $a^2 f_i(a)$ at high polyion charge density. As the added Cu^{2+} ion concentration is increased and the apparent polyion charges are decreased to the non-ion-condensation state by the masking effect of Cu^{2+} ions, the quantity $\Delta a_{Na}/(C_{Cu} - a_{Cu})$ becomes to be close to unity obeying eq. (14) as seen in the experiments.

In the case of activity expression, eq. (13) or eq. (14), the neutrality fluctuation of the free-volume, X is also ignored. This term X cannot be estimated from the activity measurements, but X is thought not to be qualitatively so large in our present solutions with low ionic strength.

It should be noted that the important character of the independence of the counterion valence in eq. (14), is attributed to the diffusion term $-kT\nabla \ln f_i$ in eq. (3) which has no valence term; the electric force term $z_i \nabla \phi$ has been converted to the terms X and $n\lambda/V$ in eq. (11).

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