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The Molal Osmotic Coefficients and Counterion Activity Coefficients of Arabate with Various Counterions[1]

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The interaction of arabic acid with counterions was studied by measuring the molal osmotic coefficients and counterion activity coefficients. The molal osmotic coefficients, ϕ, of various salt solutions were measured with a vapor pressure osmometer. In the monovalent salts, the ϕ value slightly decreased with decreasing hydration radii of counterions, but in divalent salts, the ϕ value was similar to each other and was about a half of those of monovalent salts. The counterion activity coefficients, γ_+, for Na and/or Ca arabate with or without added salts were determined by measuring electromotive force with cation-selective electrodes. In the absence of added salts, γ_+ was slightly larger than ϕ. In the presence of added salts, the additivity rule held very well for Na and Ca arabate solutions. In such a system with two kinds of counterions, Na and Ca, coexisting in arabate solution, Ca ion was preferentially adsorbed onto the polyions and consequently Na ion was less subject to the influence of the polyion. These results suggest that the interaction of arabic acid with counterions is due to the electrostatic free force alone, and not by any other specific force, and further suggest that Manning's theory for cylindrical polyelectrolytes seems to be applicable to the case of a branched polysaccharide, arabate, if the intercharge distance, "b," can be assumed to be a parameter reflecting a spatial intercharge distance.

Keywords——gum arabic; osmotic coefficient; counterion activity coefficient; Manning's theory

Gum arabic, a dried gummy exudation obtained from species of the genus *Acacia*, is widely used in the field of pharmaceuticals, foods and cosmetics as an emulsifying agent, suspending agent and/or raw material for microcapsule preparations.[2] The main component of gum arabic is arabic acid which is a branched heteropolysaccharide composed of D-galactose, L-rhamnose, L-arabinose and D-glucuronic acid. Arabic acid is an anionic polyelectrolyte since it contains glucuronic acid. As the molar fraction of glucuronic acid in arabic acid was observed to be 0.18 and its equivalent weight as measured by the neutralization method in the present experiment was found to be about 1230, it is proposed that arabic acid has one carboxyl group for every seven glycosides. The generally accepted core structure is presented in Fig. 1, where R is side chains such as L-Rha(1→, L-Ara(1→, D-Gal(1→3)-L-Ara(1→, L-Ara(1→3)-L-Ara(1→.

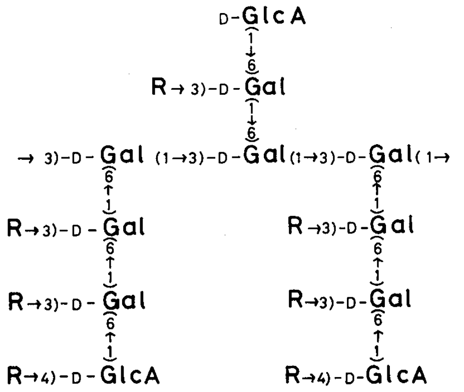

Fig. 1. Possible Core Structure of Arabic Acid

GlcA, glucuronic acid; Gal, galactose; Rha, rhamnose; Ara, arabinose.

Because of the branching as well as the low charge density of arabic acid, the theoretical investigation of arabic acid is not as easy as that of linear polysaccharides. In fact, there are many reports on the physico-chemical properties of linear polymers, but only a few studies along these lines have been reported for arabic acid in spite of its wide use in many fields as mentioned above.[3] It is important, therefore, to elucidate in detail the properties of arabic acid in order to permit its more effective utilization. It is necessary to know what molecular size of arabic acid can display the desired characteristics, and further, how its properties depend on the degree of branching, and so on.

In the present work, the osmotic coefficients and counterion activity coefficients of arabate solutions were measured to cast light on the fundamental properties of polyelectrolytes. In addition, by applying Manning's theory[4] to our results for arabate, the intercharge distance was estimated theoretically and the characteristics of arabate at infinite dilution were investigated.

Experimental

Materials——All chemicals used in this work, except for arabic acid, were of reagent grade and were used without further purification. Arabic acid was purified from a batch of crude Acacia senegal gum (Fl-08), a gift from San-ei Chemicals Engineering Co. by the following method.[5] The crude gum was dissolved in water to yield a 60 weight percent solution and filtered through a No. 2 glass filter to remove insoluble materials. Upon addition of two volumes of ethanol to the filtrate, a mixture of various arabic acid salts was precipitated. These procedures of dissolution and precipitation were repeated twice. The final precipitate was dissolved in water and treated with a mixture of cation exchange resin (Dowex 50X-4) and anion exchange resin (Dowex 1—4) to yield free arabic acid. Before use, the resin was washed repeatedly with methanol and hot water (80 °C) alternately to remove impurities as far as possible.[6] The purified arabic acid was freeze-dried and stored in a desiccator at room temperature.

Various salts of arabic acid such as $(C_4H_9)_4N$, Li, Na, Mg, Ca and Ba arabates were prepared by neutralization of the purified arabic acid with corresponding hydroxides.

Chemical Analysis of Purified Arabic Acid——Purified arabic acid was hydrolyzed in the usual way and the hydrolysate was analyzed by thin-layer chromatography (TLC).[7] Four spots were found and identified as galactose, arabinose, rhamnose and glucuronic acid. Neutral sugar contents were determined by high performance liquid chromatography (HPLC) and gas chromatography (GC). Glucuronic acid content was determined by the sulfuric acid-carbazole reaction method.[7] Sugar contents in molar ratio were found to be galactose : arabinose : rhamnose : glucuronic acid = 0.43 : 0.26 : 0.13 : 0.18, close to the values reported by Anderson *et al.*[9] Sugar analysis by HPLC was done in a usual manner on a Sorbax NH_2 column (250 × 4.6 mm i.d.). The mobile phase was acetonitrile–water (7 : 3). Gas chromatography was performed on a Yanagimoto G-80 instrument equipped with a hydrogen flame ionization detector and a glass column (150 × 3.4 mm i.d.) packed with silicone OV-17.

Characteristics of Arabic Acid and Its Salts——By potentiometric titration of arabic acid, its equivalent weight was found to be 1230 g/eq, and this value is in good agreement with published values.[2] In the analytical ultracentrifugation, the schlieren pattern of Na arabate gave a symmetrical peak. The weight-average molecular weight of Na arabate was determined by the sedimentation equilibrium method in 0.5 M NaCl, and found to be 3×10^5 daltons. The intrinsic viscosity, $[\eta]$, of Na arabate, measured with an Ubbelohde dilution viscometer in 0.5 M NaCl at 25 °C, was 17.0 ml/g.

Measurements of Molal Osmotic Coefficients——A vapor pressure osmometer, Corona type 117, was used for measuring the molal osmotic coefficients of arabate solutions at 25 and/or 60 °C. In this study, sucrose was used as a calibration standard. As the reading of the thermister bridge, ΔR, is proportional to the vapor pressure depresssion of sucrose solution, it can be expressed by the following equation,

$$\Delta R = K\phi_1 m_1 \tag{1}$$

where K is the instrumental constant, ϕ_1, the molal osmotic coefficients of sucrose and m_1, the molality of sucrose. In a low concentration range of sucrose (0.005—0.04 mol/kg). ϕ_1 can be assumed to be unity. Thus, the instrumental constant, K, was evaluated by use of Eq. (1). As the concentration of polyions of arabate required to depress the vapor pressure is sufficiently small compared to that of counterions, the molal osmotic coefficients of arabate solutions, ϕ, may be estimated from Eq. (2),

$$\phi = \Delta R/(K(m_p/z_g)) \tag{2}$$

where m_p is an equivalent concentration of arabate and z_g, the valence of counterions.

The molal osmotic coefficients of arabate solutions at 0 °C were measured by the freezing point depression method using an Advanced 3DII type osmometer.

In the mixtures of Na and Ca arabate solutions, molal osmotic coefficients were calculated by replacing z_g in Eq. (2) with the supposed average valence, z'_g. Then we obtain,

$$z'_g = \frac{n_1 + 2n_2}{n_1 + n_2} \tag{3}$$

where n_1 and n_2 are the numbers of Na^+ and Ca^{2+} ions per unit volume, respectively.

Measurement of Counterion Activity Coefficients——For Na and Ca arabate solutions, activity of counterions, a_+, was determined by measuring the electromotive force (EMF) with cation-selective electrodes. Na-ion activity was determined with an Orion combination electrode for Na, model 94-11, and Ca-ion activity was determined with an Orion Ca electrode, model 93-20. The Ca electrode was combined with an Orion single junction reference electrode, model 90-01. All EMF measurements were made with a precision potentiometer, Metrohm EA 510, in a constant-temperature water bath at 25 °C. Calibration for Na and Ca electrodes were carried out using various concentrations of aqueous NaCl and $CaCl_2$ solutions, respectively, and a linear relation of EMF *versus* $\log a_+$ was obtained. Activity coefficients of Na^+ and Ca^{2+} ions in NaCl and $CaCl_2$ standard solutions were calculated by the interpolation method, using known values of mean activity coefficients[10] γ_+, based on Guggenheim's assumption of $\gamma_\pm = \gamma_+$. Therefore, counterion activity coefficients of Na and/or Ca arabate solutions, γ_+, can be obtained by using the relation,

$$\gamma_+ = m_p/a_+ \tag{4}$$

To ensure accurate measurement of counterion activities of a mixture of Na and Ca arabate solutions, we confirmed that Ca^{2+} did not interfere with the sodium electrode, or Na^+ with the calcium electrode within the measured concentration ranges.

Results

Molal Osmotic Coefficients of Arabate Solutions

Molal osmotic coefficients of various salt solutions of arabic acid were measured at 60 °C by the vapor pressure equilibrium method. The results obtained are shown in Fig. 2, where the ordinate represents thermister bridge reading, ΔR, and the abscissa the equivalent concentration of arabate. In the case of sucrose, its concentration is expressed in molality. It is clear from Fig. 2 that ΔR of monovalent salt solutions is larger than that of divalent salt solutions. Among monovalent salts, ΔR of $(C_4H_9)_4N$ arabate was the largest, and the magnitude of ΔR was in the order of $(C_4H_9)_4N > Li > Na > K$. On the other hand, no difference in ΔR was observed among divalent salts. As for free arabic acid, H, its ΔR-*versus*-concentration relation differed greatly from that of monovalent salts, and ΔR fell between those of mono and divalent salts.

Based on the results described above, the molal osmotic coefficients of aqueous arabate solutions, ϕ, were calculated by use of Eq. (2). The results are shown in Fig. 3. It is clear that ϕ varies with kind of salts and decreases in the order of $(C_4H_9)_4N > Li > Na > K > Mg \simeq Ca$

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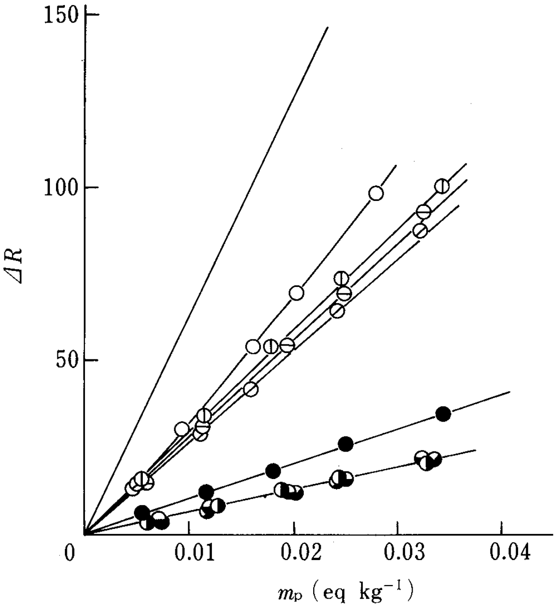

Fig. 2. Thermister Bridge Reading of Vapor Pressure Osmometer, ΔR, *versus* Concentration of Various Salts of Arabic Acid

——, sucrose; ○, $(C_4H_9)_4N$; ⦶, Li; ◒, Na; ⊘, K; ●, H; ◑, Ca; ◒, Ba; ◕, Mg.

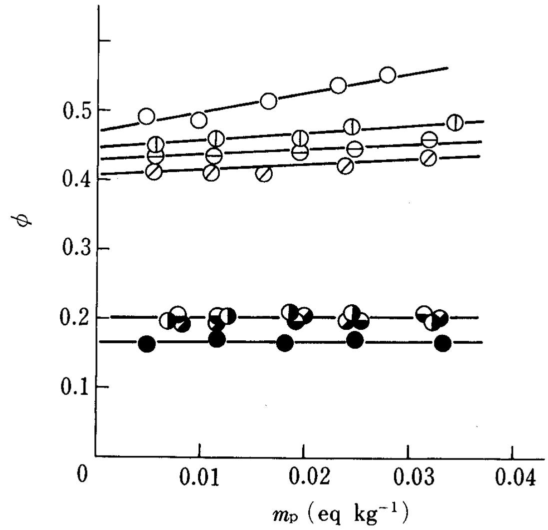

Fig. 3. Molal Osmotic Coefficients, ϕ, *versus* Concentration of Various Salts of Arabic Acid

See Fig. 2 for details.

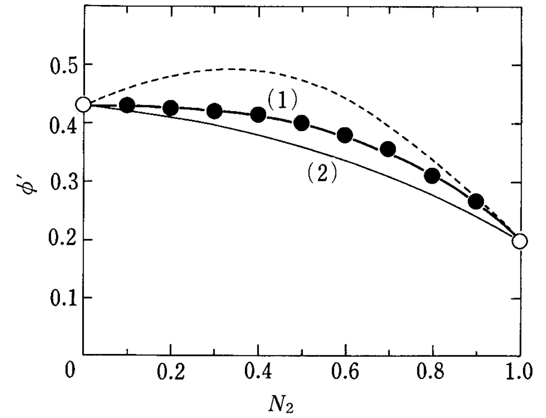

Fig. 4. Molal Osmotic Coefficients, ϕ, as a Function of Equivalent Fraction of Calcium Ions, N_2, for Mixtures of Sodium and Calcium Arabate

The broken line indicates the curve calculated on the basis of the Manning's theory.
Solid line (1) is the observed curve.
Solid line (2) is the calculated curve.

$\simeq$ Ba $>$ H. Considering that the $(C_4H_9)_4N$ ion hardly binds to the charges of polyelectrolytes because of the large size and low surface charge density of the latter molecules, it seems reasonable that $(C_4H_9)_4N$ arabate solutions showed the heighest value. In monovalent salts, the value of ϕ decreased slightly with decreasing hydration radii of counterions, but with divalent salts the values of ϕ were similar to each other and were equal to about a half of those of monovalent salts. As for concentration dependence of ϕ, it was not observed for free arabic acid or the divalent salts but it was observed for the monovalent salts.

The molal osmotic coefficients of Na and Ca arabate solutions were also determined at 25 and 0 °C. These values of ϕ were in good agreement with those at 60 °C shown in Fig. 3. Our finding of temperature independence of ϕ is consistent with the results reported for chondroitin sulfate.$^{11)}$

Molal Osmotic Coefficients of Na/Ca Arabate Mixtures

Molal osmotic coefficients of mixtures of Na and Ca arabate solutions (Na/Ca mixtures) were examined to investigate polyion-small ion interaction in mono- and divalent salt mixtures. In the present work, total arabate concentration was fixed at 0.025 eq/kg. The results obtained are shown in Fig. 4, where molal osmotic coefficients of the mixture system, ϕ' are plotted against equivalent fraction of Ca^{2+} ion, N_2, which was defined as $2n_2/(n_1+n_2)$.

In Fig. 4, the solid line (2) is a predicted one based on the assumption that the contribution of salt to the vapor pressure depression is almost the same between in the single salt solution and in the mixture system and it was obtained by replacing ΔR in Eq. (2) by $\Delta R_{Na}+\Delta R_{Ca}$, where each value was obtained from Fig. 2. Under the experimental conditions, the observed values of ϕ' were larger than those predicted by the solid line (2), but smaller than those predicted curve based on the Manning's theory indicated by the broken line.

Counterion Activity Coefficients of Na and Ca Arabate

To investigate the behavior of Na^+ or Ca^{2+} ions in each salt solution, counterion activity coefficients, γ_{Na} or γ_{Ca}, were determined by measuring the EMF with cation-selective electrodes. The results obtained are shown in Fig. 5. The value of γ_{Na} slightly increased with increasing salt concentration, but there appeared to be no distinct change in the value of γ_{Ca} within the range of concentration used, and it remained at a low value of about 0.2, which is about a half of that of γ_{Na}. In the case of Na arabate, non-linearity was noted at a very low concentration, probably due to the inhibitory effect of H^+ in the measurement of EMF. With calcium salts, such a deviation did not appear under the experimental conditions used. Similar experiments were carried out in the mixture solutions of Na and Ca arabate and the results obtained are shown in Fig. 6. The value of γ_{Na} gradually increased from about 0.4 to almost 1.0 with increasing value of N_2, the value of 0.4 being nearly equal to the value of Na arabate at the concentration of 0.025 eq/kg in Fig. 5. The value of γ_{Ca} was significantly lower than that of γ_{Na} over a wide range of N_2 and approached zero with decreasing fraction of Ca^{2+} ion in the mixture solutions. Taken together with our previous finding[12] that when $CaCl_2$ was added to $(C_4H_9)_4N$ arabate solutions, Ca^{2+} ion was preferentialy adsorbed onto the polyions, these results suggest that when two kind of counterions, Na^+ and Ca^{2+} coexist in arabate solutions, Ca^{2+} ions may be preferentially adsorbed on the polyions and consequently Na^+ ions may be less subject to the influence of the polyions. Therefore, it is considered that the disagreement between the predicted and observed values of the osmotic coefficients, seen in Fig. 4, arises from the nature of the ions, or the difference in condensation abilities of Na^+ and Ca^{2+} ions onto polyions. The condensation of Ca^{2+} ions onto the polyion should free two Na^+ ions, so

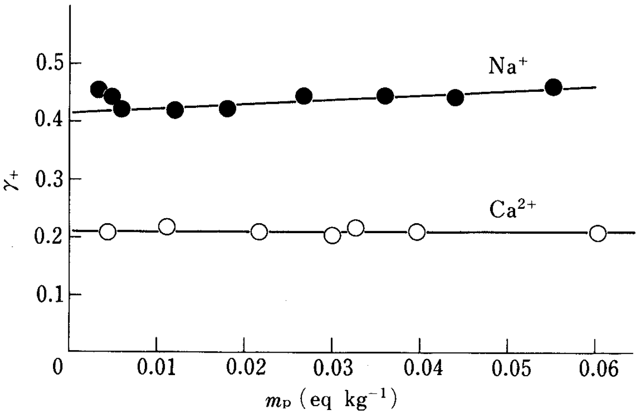

Fig. 5. Counterion Activity Coefficients, γ_+, of Na (●) and Ca (○) Arabate *versus* Concentration of Each Arabate

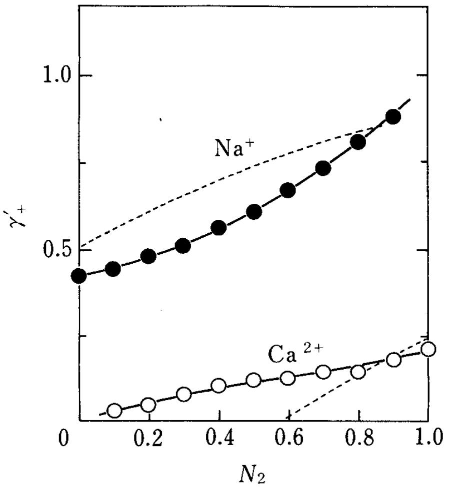

Fig. 6. Counterion Activity Coefficients, γ_+, of Na (●) and Ca (○) Arabate as a Function of Equivalent Fraction of Calcium Ions, N_2, for Mixtures of Sodium and Calcium Arabate

The broken line indicates the curve calculated on the basis of Manning's theory.

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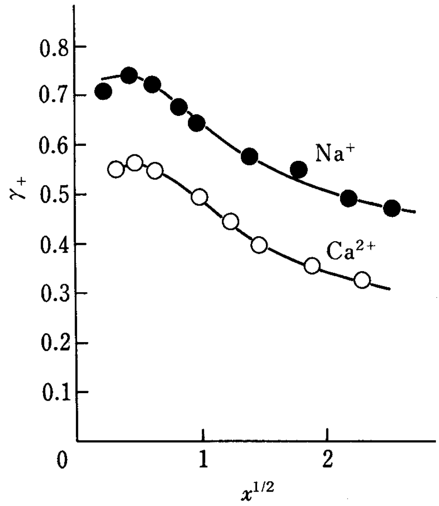

Fig. 7. Counterion Activity Coefficients, γ_+, of Na and Ca Arabate *versus* Equivalent Concentration Ratio, $x^{1/2}$, in the Presence of Added Salts

NaCl–Na Arabate system (●), $CaCl_2$–Ca Arabate system (○).

The solid line indicates the theoretical curve based on the additivity rule.

the contribution of counterions to the osmotic pressure should become larger, which is consist with our data shown in Fig. 4. With regard to the broken line in Fig. 4, which is a theoretical curve based on Manning's limiting law, there was a significant deviation between the theoretical and observed values. Although the reason for the disagreement is obscure, similar observations have been reported in mono- and divalent salt mixtures of other polyelectrolytes.[13,14)]

Activity Coefficients of Counterions for Na and Ca Arabate Solutions with Added Salts

Counterion activity coefficients of Na and Ca arabate solutions were measured in the presence of NaCl and $CaCl_2$, respectively, in order to improve our understanding of the behavior of counterions of arabate in aqueous solutions. In this experiment, the concentration of arabate was fixed at 0.01 eq/kg, and the results obtained are shown in Fig. 7. In this figure, the abscissa, x, is defined as m_p/m_s, where m_p and m_s are equivalent concentrations of arabate and added salts, respectively. In Fig. 7, each solid line indicates the theoretical curve based on the so-called "additivity rule," which is given by Eq. (5),

$$\gamma'_+(m_p+m_s)=\gamma_+m_p+\gamma_sm_s \qquad (5)$$

where γ'_+ and γ_+ are counterion activity coefficients of arabate solution with and without added salts, respectively, and γ_s is the activity coefficient of each cation in the corresponding salt solution without polymers. As is clear from Fig. 7, the experimental values were in fair agreement with the theoretical values; the deviation between them was less than 2%. These results demonstrate that the additivity rule holds very well for Na and/or Ca arabate solutions with added salts under the experimental conditions used.

Discussion

There are reports that Manning's limiting law based on cylindrical polyelectrolytes[14)] can be well applied not only to anionic polysaccharides such as Na chondroitin sulfates (NaChs)[11,15)] and Na alginate (NaAlg)[16)] but also to branched polysaccharides such as Na dextran sulfate (NaDS).[17,18)] In the present work, we investigated whether or not this theory is applicable to arabate, another branched polysaccharide.

From the findings that no marked difference in ϕ values could be detected among arabate salts of the same valence as shown in Fig. 3 and that the additivity rule held very well for mono- and divalent salts of arabic acid (Fig. 7), the interaction of arabate with counterions was demonstrate to be mainly due to electrostatic force. Provided that the interaction between

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TABLE I. The Literature Values of ϕ and γ_+ for Anionic Polysaccharides

	Degree of substitution (D.S.)	ϕ	γ_+	References
Na arabate	(0.14)[a]	0.42	0.44	Present work
Na chondroitin sulfate (NaChs)	(1)	0.45		(11)
		0.46±0.02	0.48	(15)
Na alginate (NaAlg)	(1)	0.40±0.05		(19)
Na carboxymethyl cellulose (NaCMC)	0.98	0.58±0.05	0.41	(15)
	0.95	0.58		(20)
	0.72	0.69		(20)
	0.68	0.70±0.06	0.58	(15)
Na sulfated carboxymethyl cellulose (NaSCMC)	0.78	0.62±0.05	0.45	(15)
Na dextran sulfate (NaDS)	2.54		0.228	(23)
	2.00	0.33±0.08		(17)
	1.46		0.316	(23)
	0.61		0.481	(23)

[a] Values shown in parentheses are the numbers of charged group per glucoside residue, corresponding to D.S.

polyions and counterions is due to the electrostatic force alone, the values of ϕ and γ_+ for the polyelectrolytes are well known to depend mainly on the charge density. Accordingly, the values of ϕ and γ_+ of arabate having a low charge density; one charged group for every seven glycosides were expected to be fairly large. However, the values obtained in our experiments were not as large as expected. This is probably due to the characteristic branched structure of arabate, which will be further discussed below.

Some of the literature values of ϕ and γ_+ for other anionic polysaccharides are listed in Table I. The reported values of ϕ for NaChs[11,15] and NaAlg[19] with one charged group per moiety are similar to each other. In the case of Na carboxymethyl cellulose (NaCMC), the value of ϕ changes with the degree of substitution (D.S.), *i.e.*, when D.S. was 0.95 or 0.98, its value was 0.58 and when D.S. decreased to 0.72 or 0.68, the value of ϕ increased to 0.69 or 0.70, respectively.[15,20] NaDS with a D.S. value of 2.0 shows a comparatively low value of ϕ, 0.33.[17] From these data and our finding that the ϕ value of Na arabate was about 0.42 the colligative properties of arabate seem to correspond to those of polysaccharides such as NaChs and NaAlg. It is not clear at present why the ϕ value of arabate having one charged group for seven glycosides is comparable to that of polysaccharides with one charged group per moiety. However, arabate is a branched polymer, whereas NaChs and NaAlg are linear ones.

Our attention was then drawn to an interesting report that Manning's theory for linear polyelectrolytes can also be well applied to branched polyelectrolytes such as NaDS.[17,18] We also examined whether Manning's limiting law holds in the case of arabate or not. According to Manning's theory, if a polyelectrolyte molecule is regarded as an infinitely long linear molecule on which point charges are distributed uniformly, the charge density parameters ξ can be obtained as a function of the intercharge distance, b, as follows,

$$\xi=\frac{e^2}{DkTb} \tag{6}$$

where D is the dielectric constant of the solvent, k is the Boltzmann constant, T is the absolute temperature, and e is the electric charge. At infinite dilution, ϕ and γ_+ are given by Eqs. (7)—(10).

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When $\xi \geqq z_g^{-1}$,

$$\phi = (2\xi z_g)^{-1} \tag{7}$$

and

$$\gamma_+ = (\xi z_g e^{1/2})^{-1} \tag{8}$$

and when $\xi < z_g^{-1}$,

$$\phi = 1 - \frac{1}{2} z_g \xi \tag{9}$$

and

$$\gamma_+ = \exp\left(-\frac{1}{2}\xi z_g\right) \tag{10}$$

where z_g is the valence of counterions.

In the case of arabate, it is possible to estimate the intercharge distance, b, from the structural model because of its branched structure as well as its low charge density. If the structure of arabate can be assumed to be a fully-stretched linear chain, the apparent value of b can be calculated to be 35 Å from the known structure that arabate has one charged group for every seven glycosides and the length of one glycoside is 5 Å. Accordingly, at $b = 35$ Å, ξ is given as 0.20 by Eq. (6) and at the same ξ, ϕ of Na arabate is 0.90 from Eq. (7), while γ_+ of Na arabate is 0.90 from Eq. (8). The calculated values of ϕ and γ_+ are approximately twice the experimental ones of 0.42 for ϕ and 0.45 for γ_+. Taking into account that the value of ϕ is inversely proportional to the charge-charge distance, it can be assumed that the value of b is, in practice, smaller than 35 Å. Hence, based on the experimental value of the charge density, an attempt was made to calculate the b value as follows. From Fig. 3, the ϕ value of Na arabate at infinite dilution is obtained as 0.42, which, when put into Eq. (7), gives a value of 1.19 for ξ. Substituting this value for ξ in Eq. (6) yields 6.64 Å for b.

Now, we shall assume that there are some polyelectrolytes, A and B, which have a 6.64 or a 35 Å intercharge distance, respectively. In the same manner as described above, we can calculate the values of ϕ and γ_+ with $b = 6.64$ or 35 Å. The results calculated for the polyelectrolytes with mono- and divalent counterions are presented in Table II. It is clear from Table II that the values of ϕ and γ_+ of the polyelectrolytes with $b = 6.64$ Å are very similar to those of arabate. The value of b for arabate should thus be 6.64 Å which is about one-fifth of the value of 35 Å calculated theoretically. The intercharge distance of 6.64 Å is, however, calculated on the basis of Manning's theory which applied to linear polyelectrolytes. In other words, the distance is an intercharge distance along the fully stretched linear chain. As arabate is a branched polyelectrolyte, a rather different interpretation of b is needed. There is a report that Manning's theory can be applies to polyglutamic acid, which is known to

TABLE II. The Colligative Properties of Arabates and Some Polyelectrolytes

		b/Å	ξ	z_g	ϕ	γ_+
Arabates				1	0.42	0.44
(Experimental values)				2	0.21	0.22
Polyelectrolytes	A	30	0.24	1	0.90	0.90
				2	0.80	0.82
(Calculated values)	B	6.64	1.19	1	0.42	0.51
				2	0.21	0.26

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undergo a helix-random coil transition, by regarding "b" as a spatial distance.[21] Thus, if it can be assumed that the "b" is a parameter reflecting a spatial intercharge distance, Manning's theory is thought to be applicable to the case of arabate, too.

The phenomenon that the b value calculated from ϕ or γ_+ actually observed is smaller than the b value predicted from the charge density on the basis of the fully stretched model has also been reported in cylindrical and branched polymers with $\xi < z_g^{-1}$. In the case of Na pectinate,[22] the increase in the experimental value of γ_+ estimated from the decrease in ξ is less than what is predicted by the limiting law. In particular, in Na pectinate with $\xi = 0.25$ which is similar to that of arabate, the ξ value calculated from the experimental value of γ_+ is between 0.5 and 0.65. This strongly suggests that the molecule shrinks to between 1/2 and 2/5 of the theoretical size calculated from the fully stretched formula of Na pectinate. According to Manning,[4] such a phenomenon can be explained by assuming that in low-charge-density polyelectrolytes the electrostatic repulsions between neighboring charges may not be strong enough to prevent folding of the polyelectrolyte. In a branched polyelectrolyte, NaDS with $\xi < z_g^{-1}$, the γ_+ value predicted by Manning's law is larger than that observed, and the difference between the experimental and theoretical values of γ_+ increases with decrease of the charge density.[23] It should be noted here that even at the same charge density, the magnitude of the difference in NaDS is much larger than that observed in Na pectinate. This means that the magnitude of the molecular shrinking of NaDS is larger than that of Na pectinate. This difference observed in the branched polymer, NaDS, compared to the cylindrical polymer, Na pectinate, is considered to be due to the branching. A comparison of our data for arabate with the values described above suggests that arabate at infinite dilution shrinks to give an intercharge distance of 6.64 Å, although the theoretical value of b calculated from the known structural formula is about 35 Å, which is about 5 times larger.

In the mixture system of mono- and divalent salts of arabic acid, the experimental values for ϕ and γ_+ did not fit the limiting law prediction,[21] as shown in Figs. 4 and 6. In Fig. 6, the theoretical value for γ_{Ca} drops to zero at $N_2 = 0.58$, while γ_{Ca} value decreased gradually with N_2 but at no point became zero. Further, the theoretical values of ϕ and γ_{Na} were higher than the experimental ones at any mixing ratio. These characteristics of ϕ and γ_+ in the mixed system were also found in cylindrical polymers.[13,14,24] In particular, the ϕ values of carboxymethyl cellulose (CMC) with D.S. = 1 in the mixed system showed a pattern similar to that in Fig. 6.[14] Therefore, it can be considered that the behavior of ϕ and γ_+ in the mixture of Na and Ca arabate is not specific for arabate, but is similar to that of other cylindrical polyelectrolytes.

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References and Notes

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