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Estimation of Cation Binding of Arabate by Conductivity Measurement¹⁾

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The cation binding behavior of arabate was investigated by conductivity measurements with reference to the various colligative properties of arabate reported previously. The equivalent conductance of arabic anion, A_p , was found to be about $6 (\Omega^{-1} \cdot \text{cm}^{-1} \cdot \text{eq}^{-1})$ from the conductivity titration curves of arabic acid with tetra-*n*-butylammonium hydroxide (TBA-OH). Using the value of $A_p = 6$, cation binding of arabate was estimated by the conductivity measurement of TBA-arabate at a constant concentration of 1.2×10^{-2} (eq/kg) in the presence of various added salts, and the binding curves were found to be of Langmuir type. Since the saturated amounts of cation binding, x_∞ , were observed to be similar to each other among cations of the same valency, since they increased with the valence number of cations, the interactions of arabate with cations were suggested to be due to electrostatic force. The present results are discussed in terms of the estimation methods of cation binding behavior of arabate.

Keywords—gum arabic; arabic acid; conductivity measurement; cation binding

Introduction

Arabate, which is the main component of gum arabic, is a typical polyelectrolyte, and is widely used as a food additive and a pharmaceutical material²⁾ because of its particular characteristics arising from its branched anionic heteropolysaccharide structure with a very low charge density, as discussed previously.³⁾ Among many useful characteristics of arabate, its emulsifying ability and binding capacity are excellent. In contrast to the extensive investigations on the physicochemical properties of linear polyelectrolytes, relatively little is known about arabate.

Recently, gum arabic has been in short supply worldwide because of under-production in the Republic of Sudan, which is a main producing country. Thus, it would be desirable to develop a substitute for gum arabic. First, however, the physicochemical characteristics of arabate must be established.

In the previous paper, such colligative properties of arabate as the osmotic coefficient, ϕ ,³⁾ the counterion activity coefficient, $\gamma_+^{3)}$ and the transport parameter, f ,⁴⁾ were investigated

to cast a light on the fundamental properties of the branched polyelectrolyte, and the counterion binding of arabate was elucidated in detail.

In the present work, the characteristic behavior of arabate with counterions was further studied with tetra-*n*-butyl ammonium arabate (TBA-arabate) because the interaction of the TBA ion with arabate can be neglected due to the complete dissociation resulting from the large size of the TBA ion under the present experimental conditions,^{5,6)} and so the amount of cation binding to arabate can be directly calculated by using conductivity measurement.⁷⁻⁹⁾ This method seems to be simple and convenient than the others based on the colligative properties of arabate, when comparing the cation-binding characteristics of various polyelectrolytes similar to gum arabic with those of arabate. Methods for estimation of cation binding based on the colligative properties are discussed.

Materials and Methods

Arabic acid was purified from a batch of crude Acacia senegal gum (F1-08), which was a gift from San-ei Chemicals Engineering Co., as reported previously.³⁾ TBA-arabate was prepared by adding a calculated amount of extra pure TBA hydroxide, purchased from Tokyo Kasei Co., to the purified arabic acid solution. All other chemicals were of reagent grade and were used without further purification. Water used in this experiment was twice-distilled after being passed through an ion-exchange column.

Conductivity Measurements and Cation Binding to Polyanion—Conductivity measurements were performed at $25 \pm 0.01^\circ\text{C}$ with Jones' type cells and with a Metrohm Konduktoskope E 365 B. The specific conductance of anionic polyelectrolyte solution, κ , is expressed by the following equation:

$$1000 \cdot \kappa = f \cdot m_p (A_p + A_c) \quad (1)$$

where m_p is the polymer concentration in equivalents (eq/l), f is the transport parameter, that is, the ratio of free counterion to polyanion in the electric field, A_p is the limiting equivalent conductance of polyanion and A_c is the limiting equivalent conductance of counterion. On adding a salt, C_s , to the anionic polyelectrolyte solution, some cations of the added salt will be bound to the polyanion, resulting in an increase of free counterions corresponding to pC_m , where C_m is the concentration of the bound cation and p is the cation exchange parameter with a value of less than 1.0. Then, the specific conductance in a salt-added system, κ' , is expressed as follows:

$$1000 \cdot \kappa' = (m_p f - (1-p)C_m)A_p + (m_p f + pC_m)A_c + (C_s - C_m)A_+ + C_s A_- \quad (2)$$

where A_+ is the limiting equivalent conductance of the added cation and A_- is that of the added anion. The increment of specific conductance induced by the addition of a salt to the anionic polyelectrolyte solution, $\Delta\kappa$, is therefore given by Eq. 1 and Eq. 2 as follows:

$$1000 \cdot \Delta\kappa = C_m((p-1)A_p + pA_c - A_+) + C_s(A_+ + A_-) \quad (3)$$

Equation 3 indicates that C_m can be obtained by measuring both conductance and the value of p , which is dependent on the dissociation constant. In this experiment, TBA ion was used as a counterion. As this ion cannot be bound to carboxyl groups of the polymers due to the steric hindrance arising from the large molecular size of the tetrabutyl group, f can be assumed to be nearly equal to unity, and therefore, the value of p is negligible. Substituting $p=0$ into Eq. 3, Eq. 3' is obtained:

$$C_s A_s - 1000 \cdot \Delta\kappa = C_m(A_p + A_+) \quad (3')$$

where A_s is given as $A_s = (A_+ + A_-)$.

Provided that the TBA ion can dissociate completely in such a polyanion-counterion system when arabic acid is titrated with TBA-OH, the specific conductance of the solution, κ , at any degree of neutralization, should be given by the following equation:

$$1000 \cdot \kappa = C_H A_H + C_{TBA} A_{TBA} + \alpha m_p A_p \quad (4)$$

According to Eq. 4, the contribution of a cation should be expressed as $1000 \cdot \kappa_+ = C_H A_H + C_{TBA} A_{TBA}$, and this leads to

$$1000(\kappa - \kappa_+) = \alpha m_p A_p \quad (5)$$

When the values of C_H , C_{TBA} , A_H and A_{TBA} are found, A_p can be obtained according to Eq. 5.

Results

Estimation of Equivalent Conductance of Arabic Acid

To obtain the value of the equivalent conductance, Λ_p , according to Eq. 4 described in Materials and Methods, arabic acid was titrated with TBA-OH or NaOH and the pH and conductance changes were measured against the degree of neutralization, α , at a constant arabic acid concentration of 0.0162 (eq/kl). The results obtained are shown in Fig. 1. The pH titration curves of arabic acid with TBA-OH or NaOH were approximately the same at all degrees of neutralization, indicating similar degrees of ionization for both counterions. Conductometric titration curves, which are also shown in Fig. 1, were both gently concave as is characteristic of weak acids, but not strong acids, whose conductances show a linear decrease with neutralization and a sharp increase after $\alpha=1.0$. However, a different counterion showed a remarkably different titration curve, due mainly to the difference of equivalent conductances. By using the pH and conductometric titration curves shown in Fig. 1, and the literature values¹⁰⁾ of Λ_H and Λ_{TBA} , which are 349.8 and 19.5, respectively, the equivalent conductance, Λ_p , given by Eq. 4 was calculated graphically (Fig. 2). Here, $(\kappa - \kappa_+)$ and Λ_p were plotted against α , where $(\kappa - \kappa_+)$ is the difference between the observed specific conductance of the polymer-counterion system (κ) and that of the counterion alone (κ_+).

As is clear from Fig. 2, the value of $(\kappa - \kappa_+)$ increased sharply at a lower degree of neutralization and became constant at about $\alpha=0.3$. On the other hand, the value of Λ_p decreased gently with neutralization, became constant with an extrapolated value of 6.0 ($\Omega^{-1} \cdot \text{cm}^{-1} \cdot \text{eq}^{-1}$).

Specific Conductance of Arabate in a Salt-Added System and Cation Binding

The conductance of TBA-arabate solution was measured in the presence of KCl, NaCl, LiCl, CaCl_2 , BaCl_2 , MgCl_2 and LaCl_3 . In the present experiments, the final concentration of arabate was always kept constant at 1.2×10^{-3} (eq/l).

First, the specific conductance of arabate solution, κ , was measured in the presence of monovalent salts, and the results obtained are shown in Fig. 3. It is clear that the value of $\Delta\kappa$

Fig. 1. pH and Conductometric Titration Curves of Arabic Acid

(○, ●), neutralized with tetrabutylammonium hydroxide; (○, ●) neutralized with sodium hydroxide.

Fig. 2. Apparent Specific Conductance of Arabic Ion ($\kappa - \kappa_+$), and Equivalent Conductance of Arabic Ion, Λ_p , as a Function of Degree of Neutralization

Each value was calculated from the conductometric titration curve of arabic acid with TBA-OH shown in Fig. 1.

Fig. 3. Increment of Specific Conductance of Arabate-Salt Solutions versus Added Salt Concentration

The broken lines indicate the specific conductance of corresponding simple salt solutions in the absence of polymer. m_p , 1.2×10^{-2} eq/l; (○, ●), KCl; (○, ●), NaCl; (○, ●), LiCl.

Fig. 4. Increment of Specific Conductance of Arabate-Salt Solutions versus Added Salt Concentration

The broken lines indicate the specific conductance of corresponding simple salt solutions. m_p , 1.2×10^{-2} eq/l; (○, ●), CaCl₂; (○, ●), MgCl₂; (○, ●), BaCl₂; (○, ●), LaCl₃.

(solid line) increased linearly with increasing concentration of monovalent ion over the added salt concentration range from 1.5×10^{-3} to 1.2×10^{-2} (N). The slopes of the linear plots were in the order of $K > Na > Li$, reflecting the difference in the degree of association. The broken lines in Fig. 3 show the observed specific conductances of the corresponding simple salt solutions in the absence of arabate. The results indicate that the degree of binding of monovalent cations to arabate increased with increasing concentration of added salt, since the conductance difference between the solid line and the corresponding broken one may be due to the binding of the added cation to arabate.

Next, in the presence of divalent and trivalent salts, the specific conductance of arabate solution, κ , was measured at various concentrations of added salts, C_s . The results obtained are shown in Fig. 4.

The specific conductances increased linearly with C_s at low concentrations of added salts and bended up near the middle concentration tested in the present experiments so that the slopes of the solid lines got close to those of the broken lines which show the specific conductance of the corresponding simple salt solution in the absence of arabate. This may be mainly due to the saturation of cation binding to arabate, as will be discussed below.

As for the cation binding, the differences between the slopes of the solid lines and the corresponding broken ones in Fig. 4 as compared with those of Fig. 3 strongly suggest that the amount of monovalent cation binding to arabate is less than that of divalent or trivalent cations.

To clarify the characteristics of cation binding to arabate, the amount of binding, C_m , of the cation to arabate in relation to C_s was calculated according to Eq. 3 in Materials and Methods, by using the observed values shown in Fig. 3 and Fig. 4. In the use of Eq. 3', literature values of limiting equivalent conductance of various cations were taken from Robinson and Stokes¹⁰: K, 73.5; Na, 50.1; Li, 38.7; Ca, 59.5; Ba, 63.6; Mg, 53.1; La, 69.7. The value of $C_s A_s$ was obtained by measurement. The results obtained are shown in Fig. 5,

Fig. 5. The Relation between the Amount of Bound Cations, C_m , and the Concentration of Added Salt, C_s
 $\circ$, LaCl_3 ; $\bullet$, BaCl_2 ; $\bullet$, CaCl_2 ; $\bullet$, MgCl_2 ; $\ominus$, NaCl ; $\oplus$, KCl ; $\otimes$, LiCl .

Fig. 6. Increment of Specific Conductance of Arabate- CaCl_2 Solutions versus Added CaCl_2 Concentration at Various Arabate Concentrations

Arabate concentration, m_p (eq/l): 1, 1.24×10^{-2} ; 2, 8.3×10^{-3} ; 3, 5.3×10^{-3} ; 4, 1.7×10^{-3} .

The broken line (1) indicates the specific conductances of CaCl_2 solutions and the broken line (2) shows the conductivity contribution of Cl^- ions.

where the amount of bound cation is plotted against the concentration of the added salts. Each curve was of typical Langmuir type, and the saturated amount of cation bound to arabate was dependent on the cationic valences in the order of $\text{La}^{3+} > \text{Ba}^{2+} > \text{Ca}^{2+} \simeq \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+ > \text{Li}^+$.

Considering that the broken line in Fig. 5 reflects complete cation binding to arabate, it is clear from Fig. 5 that at very low concentrations of added salts, divalent and trivalent cations were bound to arabate completely but monovalent cations were not.

Dependency of Degree of Cation Binding on Arabate Concentration

The effect of arabate concentration on the cation binding to arabate was examined in the cases of NaCl and CaCl_2 . In Fig. 6, the specific conductance of arabate solution at various concentrations is plotted against the concentration of CaCl_2 . The broken line (1) in Fig. 6 shows the specific conductance of CaCl_2 solution in the absence of arabate and the broken line (2) gives the conductivity contribution of Cl^- ion in the specific conductance of CaCl_2 solution. In the relatively low concentration range of C_s , the values, $\Delta\kappa$, of various arabate solutions were approximately in agreement with the broken line (2), which means that in these regions almost all of the added calcium ions were bound to arabate.

The amount of calcium bound to arabate was calculated at various concentrations of arabate with use of Eq. 3', and the results obtained are shown in Fig. 7, where C_m is plotted against C_s . At all concentrations of arabate, the binding curves seemed to be of Langmuir type because of the saturation. The numerical values of x_∞ and k at various arabate concentrations, m_p , were therefore calculated in the presence of CaCl_2 and NaCl based on the Langmuir-type binding curve given by the following equation,

$$x = \frac{x_\infty \cdot k C_f}{1 + k C_f} \quad (6)$$

Fig. 7. The Relation of the Amount of Bound Cations C_m and the Concentration of CaCl_2 at Various Arabate Concentrations

Arabate concentration, m_p (eq/l): 1, 2.49×10^{-3} ; 2, 1.66×10^{-2} ; 3, 1.24×10^{-2} ; 4, 8.3×10^{-3} ; 5, 3.3×10^{-3} ; 6, 1.7×10^{-3} .

Fig. 8. Degree of Cation Binding to Arabate Estimated by Conductivity Measurement, x_x

●, NaCl; ○, CaCl_2 .

TABLE I. Numerical Values of x_x and k in Eq. 6 at Various Arabate Concentrations, m_p , in the Cases of NaCl and CaCl_2

Added salt	m_p (eq/l)	k	x_x (mol/eq)
CaCl_2	2.49×10^{-2}	1.05	0.40
	1.66×10^{-2}	1.16	0.43
	0.83×10^{-2}	2.50	0.50
	0.33×10^{-2}	4.24	0.59
	0.17×10^{-2}	3.68	0.68
NaCl	1.25×10^{-2}	0.34	0.25
	0.66×10^{-2}	0.34	0.28
	0.33×10^{-2}	0.69	0.33

where k is the binding constant, C_r is the equilibrium concentration of added salt, x is the amount of binding defined as $x = C_m/m_p$ and x_x is the saturated amount of binding. The results are presented in Table I. These results are illustrated graphically in Fig. 8, where the saturated amounts of sodium and/or calcium, x_x , are plotted against arabate concentration. As is clear from Fig. 8, x_x increased gradually with decreasing arabate concentration.

Discussion

We have investigated the conductometric behavior of TBA–arabate and found that the binding characteristics of arabate with the counterions were of Langmuir type, indicating that the interaction was due to the electrostatic force. This result is fundamentally in good agreement with the results reported in the previous papers.^{3,4)} From these results, it is possible to estimate the degree of cation binding to arabate. As shown in Fig. 9, in the cases of Na^+ and Ca^{2+} as a mono- and divalent cations, respectively, the degrees of cation binding to arabate were not always in good agreement with each other. The reasons for this may be differences in the methods of estimation based on various parameters such as the counterion activity coefficient, γ_+ , the osmotic coefficient, ϕ , the transport parameter, f , and the saturated amount of cation binding, x_x . This point will be discussed below.

Fig. 9. Degree of Cation Binding for Arabate Estimated from Various Measurements

Calcium, a, $1-\phi$; b, $1-\gamma_+$; c, $1-f$
Sodium, a', $1-\phi$; b', $1-\gamma_+$; c', $1-f$

The broken lines indicate the x_x values from Fig. 8.

Among these parameters, γ_+ and ϕ are obtained from an assay system based on the thermodynamic characteristics of arabate, whereas, f and x_x are obtained from conductivity measurements. Thus, the values of $(1-\gamma_+)$ and $(1-\phi)$ shown in Fig. 9, will be essentially equivalent. It is also suggested that $(1-f)$ will be roughly equivalent to x_x . In fact, the degree of Na^+ binding to arabate was, as expected, in the order of $x_x \simeq (1-f) < (1-\gamma_+) \simeq (1-\phi)$. In the case of Ca^{2+} , however, unexpected results were obtained. That is, x_x was smaller than $(1-f)$ and the degree of binding was in the order of $x_x < (1-f) < (1-\gamma_+) \simeq (1-\phi)$.

Although the reasons for such a marked difference between x_x and $(1-f)$ are not clear at present, the different experimental conditions used may be involved. The value of f was obtained by the conductivity measurement of arabate solution in the absence of added salts. In this case, the value of the equivalent conductance of arabic anion, A_p , was determined by the transference measurement as $A_p = 4.4$. On the other hand, the value of x_x was obtained by the conductivity measurement of arabate solution in the presence of added salts as $A_p = 6$. Considering that the value of A_p is reported to depend on the type of counterion,¹¹⁾ different counterions will give different values of A_p . In our experiments, sodium arabate was used for the transference measurement and TBA-arabate for the conductivity measurement. The difference may be attributable to the low value of x_x compared to $(1-f)$, as shown in Fig. 9.

In addition, the different ionic strength brought about by the absence or presence of added salts may be one of the more important factors affecting the degree of cation binding. In the present work, as in the work on $(1-f)$ reported previously, the literature value of A_+ at infinite dilution was used because it is impossible to get an accurate value at finite concentration in the presence of added salts in addition to polyelectrolyte. It is well known that the equivalent conductance of an electrolyte solution is dependent on the ionic strength and that this dependency is much larger in a polyvalent salt system than in a monovalent salt one. Therefore, at such a high ionic strength as used in the present work, the practical value of A_+ should be smaller than the literature value used, and the deviation would be larger in the case of CaCl_2 than NaCl .

In the present work, we investigated the cation binding behavior of arabate by the conductivity measurement with reference to the various colligative properties of arabate, and found that the behavior estimated from any one of the 4 parameters was essentially the same in the concentration ranges tested. This is because for both Na^+ and Ca^{2+} , as shown in Fig. 9, the broken lines indicating the conductivity measurements and the solid lines indicating the others were parallel to each other except at very low concentrations of added salts. This good relationship seems to be very important when arabic acid-like substances are to be selected from among various polyelectrolytes and polysaccharides similar to gum arabic, because this conductance titration method is very simple and can be carried out easily without any special techniques or instruments. Therefore, we believe that this method may have some advantages

over the other three methods, at last in the preliminary experiments.

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