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STUDIES ON THE INTERACTION BETWEEN ALKALI METAL CATIONS AND POLYION BY SOUND VELOCITY

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The sound velocities in polyelectrolyte solutions were measured at various concentrations of added salts. When aqueous solutions of tetra(*n*-butyl)ammonium polyacrylate were titrated with concentrated solutions of LiCl, NaCl, KCl or CsCl, the sound velocity, i.e., the adiabatic compressibility of the solution, did not change linearly with added salt concentration, but showed a breaking point. The degrees of counterion binding on polyacrylate ion estimated from the breaking points were 0.25–0.30, independent of cation species. In polystyrenesulfonate, moreover, no Na^+ binding was detected from such sound velocity measurements.

1. Introduction

It is well known from the thermodynamic properties of a polyelectrolyte solution, such as the activity coefficient and osmotic pressure, as well as from transport properties of the solution, that alkali metal counterions strongly interact with polyions, such as polyacrylate and polystyrenesulfonate, as if they are bound on the polyions [1,2]. However, the interaction between polyions and alkali metal ions has not been specified spectroscopically [1,2]. We also confirmed from Raman spectroscopy [3,4] that there is no spectroscopically specific interaction between polyacrylate ion and alkali metal ions, though a specific interaction can be clearly observed between polyacrylate ion and some divalent counterions.

On the other hand, from the viewpoint of the hydration around polyions and counterions, for example, from measurements of density [4–8], refractive index [9], sound absorption [10], and volume changes by dilatometry [11–13] in polyacrylate solutions, a specific interaction between polyacrylate ion and alkali metal ions has been demonstrated by several workers. That is, it may be certain that part of the alkali metal counterions are attracted as closely to the polyacrylate ion as the hydration layer around the polyion may be affected. However, the degrees of specific binding (θ) of alkali metal ions on polyacrylate ion reported in these papers vary considerably with different methods. For Na^+, values of $\theta = 0.22$ from the partial molar volume data [7] and $\theta = 0.69$ from the refractive index data [9] were reported.

In this work, we study the hydration layers around polyion and counterions or the overlapping of their hydration layers by measuring the sound velocity in polyelectrolyte solutions. From the data, the degree of counterion binding on polyion may be estimated by using a procedure employed commonly in this field [8]. The sound velocity, which is related to the adiabatic compressibility of the solution of the Laplace equation, may be most sensitive to the change in the hydra-

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tion volumes around ions, particularly to that in the first hydration shell. The adiabatic compressibility of polyelectrolyte solutions was investigated by Roy-Chowdhury and co-workers [14,15] in order to study the properties of polyions.

2. Experimental

2.1. Samples

A sodium polyacrylate sample supplied by Toa Gosei Chemical Co. was purified by precipitation from aqueous solution with methanol. Sodium polyacrylate was transformed into the acid form by passing its aqueous solution through a mixed-bed column of ion-exchange resins. Its molecular weight estimated from the intrinsic viscosity [16] was 3×10^5. Tetra(*n*-butyl)ammonium polyacrylate was prepared by neutralization of poly(acrylic acid) with an aqueous solution of $(n\text{-}C_4H_9)_4NOH$ (of reagent grade). The polystyrenesulfonic acid sample used was commercially supplied from Polysciences, Inc. ($M_r = 7 \times 10^4$). 18-Crown-6, used as reference, was purified by the procedure proposed by Gokel and Cram [17]. All simple salts were of guaranteed reagent grades and were used without further purification.

2.2. Sound velocity measurement

The sing-around method was employed to measure the sound velocity. Since the sing-around frequency is very sensitive to temperature, the ultrasonic velocimeter consisted of two cells. One cell was for sample solutions, whereas the other contained pure water used as a reference. Experiments were carried out at 25.00 ± 0.001°C and the accuracy in measurements of sound velocity was within 1.0 cm s^{-1}. A detailed description of the original sing-around apparatus has been presented elsewhere [18,19].

To prepare sample solutions containing different amounts of a simple salt, such as NaCl, a concentrated solution of the simple salt was added to an aqueous solution of tetra(*n*-butyl)ammonium polyacrylate with a microburette as in the case of acid-base titration. The sound velocity of the solution was measured at each addition. Changes in polyacrylate concentration accompanying the titration were within 1%. No correction for the dilution effect was made to the experimental data.

2.3. Adiabatic compressibility

The sound velocity in solution, V (m s^{-1}), is related to the compressibility of the solution, β_s (bar^{-1}), by

$$\beta_s = 100/V^2d \tag{1}$$

where d (g ml^{-1}) is the density of the solution.

Solution density was measured at 25.00 ± 0.001°C, using a type DMA-02C digital precision density meter manufactured by Anton Paar Co. The density of each sample solution used for sound velocity measurements was estimated by interpolation.

3. Results

Fig. 1 shows the sound velocity and density of an aqueous solution of KCl at different concentrations in the presence and absence of 18-crown-6.

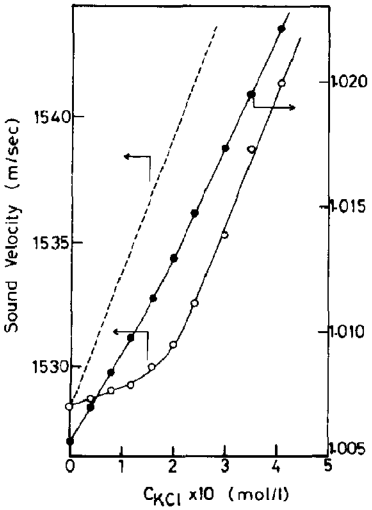

Fig. 1. Sound velocity and density in mixed aqueous solutions of KCl and 18-crown-6 at various KCl concentrations. Concentration of 18-crown-6, 0.2 mol/l. (------) Data in aqueous KCl solution in the absence of 18-crown-6.

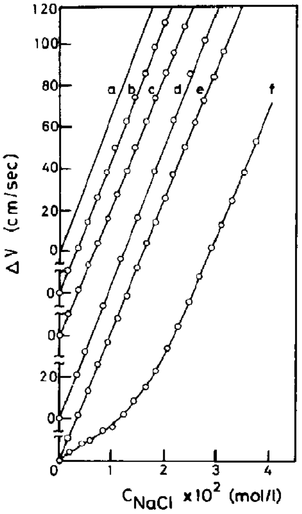

Fig. 2. Increase in sound velocity, ΔV, in aqueous solutions containing various solutes with addition of NaCl. (a) Pure water, (b) acetic acid, (c) tetra(*n*-butyl)ammonium acetate, (d) poly(acrylic acid), (e) sodium polyacrylate and (f) tetra(*n*-butyl)ammonium polyacrylate. Concentration of solute, 0.05 mol/l in all cases.

The sound velocity in pure aqueous solutions of KCl changes linearly with concentration. However, the slope of the plot of sound velocity vs. KCl concentration in the presence of 18-crown-6 shows a discontinuous change around 0.2 mol/l KCl, that is, at 1 : 1 mole ratio. Above this concentration the slope for the mixture is in good agreement with that for a pure aqueous solution of KCl.

The increases in sound velocity, ΔV, observed when aqueous solutions of acetic acid, tetra(*n*-butyl)ammonium acetate, poly(acrylic acid), sodium polyacrylate and tetra(*n*-butyl)ammonium polyacrylate are titrated with a concentrated solution of NaCl, are shown in fig. 2. ΔV is defined as

$$\Delta V = V - V_0 \qquad (2)$$

where V and V_0 are the sound velocities in the presence and absence of NaCl, respectively. In acetic acid and tetra(*n*-butyl)ammonium acetate

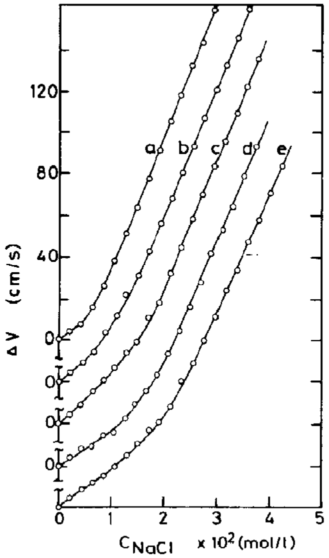

Fig. 3. Increase in sound velocity, ΔV, in tetra(*n*-butyl)ammonium acrylate solutions at different concentrations, with addition of NaCl. Polyelectrolyte concentrations: (a) 0.02, (b) 0.03, (c) 0.04, (d) 0.05 and (e) 0.06 mol/l.

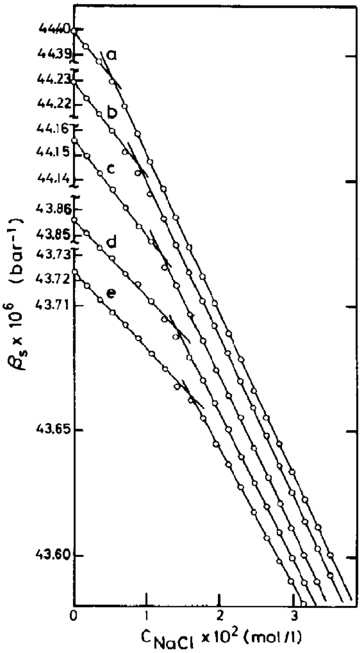

Fig. 4. NaCl concentration dependence of adiabatic compressibility of polyacrylate solutions. Concentrations of tetra(*n*-butyl)ammonium polyacrylate: (a) 0.02, (b) 0.03, (c) 0.04, (d) 0.05 and (e) 0.06 mol/l.

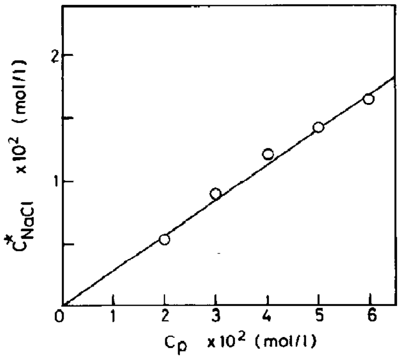

Fig. 5. Plot of NaCl concentration at the breaking point in fig. 4 vs. polyacrylate concentration.

solutions, ΔV is linear with respect to NaCl concentration. Moreover, in poly(acrylic acid) and sodium polyacrylate as well, the behavior of ΔV is the same. In these four solutions, therefore, there is no specific interaction between added NaCl and the other solutes. On the other hand, in aqueous solutions of tetra(n-butyl)ammonium polyacrylate, ΔV is not linear with NaCl concentration. The slope of the plot of ΔV vs. NaCl concentration is low at the beginning of titration and gradually increases to the value for a pure aqueous solution of NaCl. Fig. 3 shows similar ΔV vs. NaCl concentration plots in tetra(n-butyl)ammonium polyacrylate solutions at different polymer concentrations. This NaCl concentration dependence of ΔV in polyacrylate solutions is very similar to that in the mixture of KCl and 18-crown-6.

Table 1

The values of C_s^*/C_p determined from fig. 6 and the degree of ion binding reported by Tondre and Zana [7]

	C_s^*/C_p	Degree of ion binding [7]
LiCl	0.26	0.21
NaCl	0.28	0.22
KCl	0.26	0.22
CsCl	0.26	0.11

The adiabatic compressibility, β_s, can be calculated from eq. 1 using the data in fig. 3. The values of β_s obtained are plotted vs. NaCl concentration in fig. 4. The plots also do not give simple straight lines but show breaking points. If we assume that all Na^+ added is bound on the polyion until the binding reaches a certain value and also that the change in β_s is due to the change in the hydration layer around sodium polyacrylate, the amount of

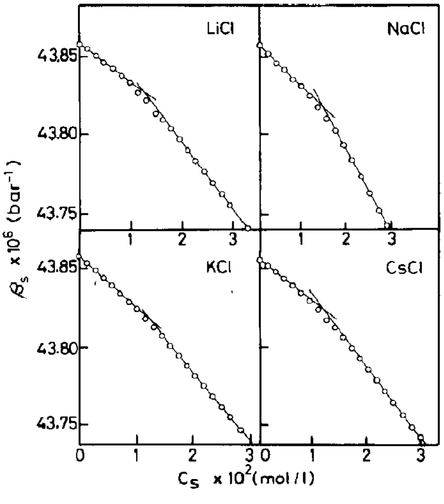

Fig. 6. Salt concentration dependence of adiabatic compressibility of tetra(n-butyl)ammonium polyacrylate solution containing various simple salts. (a) LiCl, (b) NaCl, (c) KCl and (d) CsCl. Polyacrylate concentration, 0.05 mol/l.

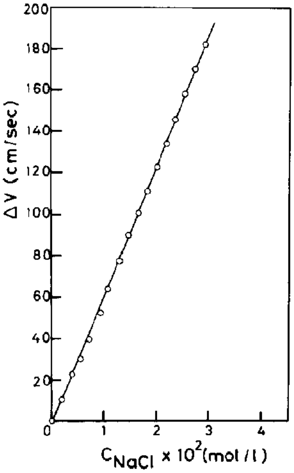

Fig. 7. Increase in sound velocity, ΔV, in aqueous solution of tetra(n-butyl)ammonium polystyrenesulfonate with addition of NaCl. Polyelectrolyte concentration, 0.05 mol/l.

Na^+ bound on the polyion may be estimated from the amount of NaCl added up to the breaking point. The NaCl concentration at the breaking point, C^*_{NaCl}, determined graphically in fig. 4 is plotted vs. the polyelectrolyte concentration, C_p, in fig. 5. The plot is linear within experimental error, and the C^*_{NaCl}/C_p ratio is 0.28 ± 0.04.

The effects of different alkali salts on β_s of tetra(*n*-butyl)ammonium polyacrylate solutions are shown in fig. 6. The values of C_s^*/C_p determined by the above method are 0.25–0.30, independent of the cation species as summarized in table 1. These values are close to those determined from the partial molar volume data by Tondre and Zana [7], as compared in table 1. However, these values (0.25–0.30) are much lower than the value estimated from the refractive index (0.69) [9]. Our values are also different from the degrees of ion binding discussed commonly in studying the thermodynamic and hydrodynamic properties of polyelectrolytes.

Fig. 7 shows the increases in sound velocity, ΔV, in an aqueous solution of tetra(*n*-butyl)ammonium polystyrenesulfonate as a function of NaCl concentration. ΔV is linear with NaCl concentration and no breaking point is observed, although it is clear from various experiments that there is a strong thermodynamic or electrostatic interaction between Na^+ and polystyrenesulfonate ion [20–22]. The absence of dehydration due to interaction of alkali metal ions with polystyrenesulfonate ion was pointed out by Strauss and Leung [23].

4. Discussion

The complex formation between 18-crown-6 and simple ions can be expressed as,

$$M^+ + X^- + C \rightleftarrows CM^+ + X^- \qquad (3)$$

where M^+ is the cation of a salt, MX, and C denotes 18-crown-6. Using the equilibrium constant for the above equilibrium, and also assuming that the change in the adiabatic compressibility of a 18-crown-6 solution containing a simple salt may be ascribed only to the changes in the hydration number of the added simple salt, Hoiland et al. [24,25] successfully analyzed the above equilibrium. It may be concluded that a 1 : 1 complex is formed between 18-crown-6 and K^+ and that the change in slope of the sound velocity vs. KCl concentration plot in fig. 1 is due to the complex formation.

Although the application of the theory of Hoiland et al. to the polyelectrolyte data in figs. 2 and 3 cannot reproduce the experimental results, there is a good resemblance between the data for complex formation between the crown ether and K^+ in fig. 1 and those for tetra(*n*-butyl)ammonium polyacrylate in figs. 2 and 3. It is usually assumed that the hydration layer around the polyacrylate ion is not disturbed by the tetra(*n*-butyl)ammonium ion because of its large size, but is affected by Na^+ bound on the polyacrylate ion, until the degree of ion binding reaches saturation. According to Zana and Tondre [26], however, there may be volume changes due to the interaction between polyion and tetra(*n*-butyl)ammonium ion, though no volume change is detected if the tetramethylammonium ion is used instead of tetra(*n*-butyl)ammonium. If their conclusion is correct, the decrease in the hydration layer around the polyacrylate ion caused by the effect of tetra(*n*-butyl)ammonium ions would be recovered when alkali metal ions are bound on the polyacrylate ion. Then, the change in adiabatic compressibility of the solution in figs. 4 and 6 includes both changes in the hydration layer around the polyion due to binding of alkali metal ion and release of tetra(*n*-butyl)ammonium ion. If there is a change in the hydration layer around Na^+, the change may also be included in β_s.

The increase in adiabatic compressibility of the solution due to addition of neutral salt, expressed per mole of added salt, $\phi_{\beta x}(MX)$, may be calculated from the slopes in the β_s vs. C_s plots in figs. 4 and 6, as

$$\phi_{\beta x} = \frac{1000}{C_s}(\beta_s - \beta_0) + \beta_0 V_s \qquad (4)$$

where C_S denotes the molarity and V_s the apparent molar volume of added salt in polyelectrolyte solution. β_s and β_0 are the adiabatic compressibilities of the polyelectrolyte solution with and without added salt, respectively. $\phi_{\beta s}(MX)$ in eq. 4 is expressed using the same definition as for the molar adiabatic compressibility of an electrolyte in aqueous solutions. The values of $\phi_{\beta s}$(MX) thus estimated are plotted vs. $\sqrt{C_s}$, in fig. 8, as is usually done in the study of the adiabatic compressibility of simple electrolyte solutions. If it is assumed that added cations are all bound to polyion at low salt concentrations, $\phi_{\beta s}$(MX) at the limit of $C_s = 0$ gives the change in adiabatic compressibility of the solution due to a bound ion (expressed per mole, $\bar{\phi}^{b}_{\beta s}$(MX)). The values of $\bar{\phi}^{b}_{\beta s}$(MX) estimated from fig. 8 are summarized in table 2. The values of the partial molar adiabatic compressibilities of a simple salt in the free state, $\bar{\phi}^{f}_{\beta s}$(MX), are also listed in table 2. If ions in aqueous solutions are incompressible, the partial molar adiabatic compressibility, $\bar{\phi}_{\beta s}$(MX), is related to the hydration number, n_h.

$$\bar{\phi}_{\beta s} = -n_h \beta_{H_2O} \bar{V}_{H_2O} \tag{5}$$

where β_{H_2O} and $\bar{V}_{H_2O}$ are the adiabatic compressibility and partial molar volume of pure water, respectively. Therefore, the difference between $\bar{\phi}^{b}_{\beta s}$(MX) and $\bar{\phi}^{f}_{\beta s}$(MX), $\Delta\phi$, provides the number of released water molecules around ions in this specific ion-binding process. As listed in table 2, the large absolute values of $\Delta\phi$ indicate that a large volume change occurs in the hydration layer around a polyion. If we express $\Delta\phi$ as the number of water molecules released, the value of the released water is about 3–4 as shown in table 2.

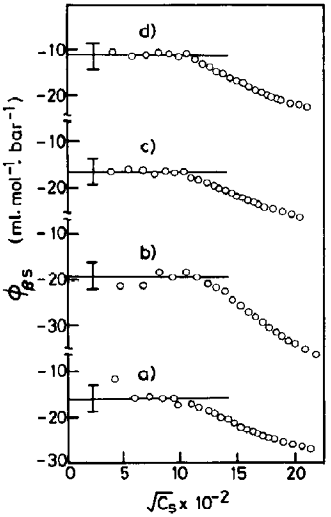

Fig. 8. Concentration dependence of the apparent molar adiabatic compressibility of various added salts in tetra(*n*-butyl)ammonium polyacrylate. (a) LiCl, (b) NaCl, (c) KCl and (d) CsCl. Polyacrylate concentration, 0.05 mol/l.

Table 2

Change of adiabatic compressibility of tetra(*n*-butyl)ammonium polyacrylate solution by addition of salts and the number of released water molecules, Δn_h

Values are expressed as cm^3 mol^{-1} bar^{-1} ($\times 10^4$).

Added salt	$\bar{\phi}^{b}_{\beta s}$	$\bar{\phi}^{f}_{\beta s}$	$\Delta\phi$	Δn_h
LiCl	−16	−40.0	−20	3.0
NaCl	−20	−50.8	−31	3.8
KCl	−16	−42.6	−27	3.3
CsCl	−11	−35.3	−24	3.0

According to Meurer et al. [27], the ^{23}Na relaxation rate in solution of the tetramethylammonium salt of polyacrylic acid changes continuously with the concentration of added NaCl. On the other hand, fig. 8 shows that the plots of $\phi_{\beta s}$(MX) vs. $\sqrt{C_s}$ at low salt concentrations are almost linear. This difference cannot necessarily be considered as a contradiction, since the contribution of the interaction between polyion and counterions to the ^{23}Na relaxation rate is different from that to $\phi_{\beta s}$.

If we assume that all alkali metal ions added to a tetra(*n*-butyl)ammonium polyacrylate solution are bound on the polyion until the degree of ion binding reaches saturation, the values of C_s^*/C_p in fig. 5 and table 1 give the degree of ion binding on the polyacrylate ion. The present data show that the degree of ion binding thus defined is not large, i.e., 0.25–0.30. This degree of ion binding is considerably lower than that assumed for explaining the nonideal thermodynamic properties of polyelectrolyte solutions or the transport number of counterion and polyion. (The degree of counterion binding in these cases is generally assumed to be 0.6–0.9 [1,2].) This means that a considerable part of the counterions in polyelectrolyte solutions are distributed loosely around the polyions so that it may often be called ionic atmospheric binding. Only a small portion of the counterions are distributed close to the polyacrylate ion so that its hydration layer may be affected.

Moreover, it is not appropriate to define a group of counterions detected by the change in hydration volume as bound ions, since the degree of ion binding thus defined must be varied with the hydration volume of the polyion used. In the case of polystyrenesulfonate, no change in hydration volume can be observed as shown in fig. 7. The polystyrenesulfonate ion may have a loose hydration layer.

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