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Studies on the interaction between polyion and counterions by sound velocity (II)

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Sound velocities in polyacrylate solutions neutralized by tetraalkylammonium hydroxide were measured at various concentrations of added NaCl. From the results, the degree of counterion binding to polyion and the extent of the changes in hydration volume due to ion binding were determined as a function of the degree of neutralization, α. The ion binding accompanying the volume changes appeared above about $\alpha = 0.6$ and the ion binding process depended on the charge density of the polyion. The effect of the size of the tetraalkylammonium ion on ion binding was negligibly small.

1. Introduction

In previous papers, we investigated the interaction between polyacrylate ion and counterions by means of Raman spectroscopy [1,2] and sound velocity measurement [3]. The results indicated that the sound velocity and adiabatic compressibility of polyacrylate solution are very sensitive to changes in the interaction accompanying the hydration volume changes. For fully neutralized polyacrylate solution, it was found that 30% of the counterions are distributed so close to the polyacrylate ion that its hydration layer may be affected.

It is well known that a fraction of the counterions bound to a polyion depends on the charge density [4–6]. In general, in the estimation of this fraction, it is difficult to distinguish counterions which are attracted to polyion by the specific interaction from those attracted by the ion atmospheric interaction. Here, specific interaction refers to the interaction between polyion and counterions accompanying volume changes around ions. Using measurement of sound velocity, it is possible to estimate the fraction of counterions bound to polyion due to the specific interaction as a function of the charge density.

The proper choice of reference ion is an important consideration in estimating the fraction of counterions bound to polyion and the extent of the changes in hydration volume. Ions to be chosen as reference ions should interact negligibly with the polyion. In general, tetraalkylammonium (TAA^+) ions have been chosen as reference ions because of their large size, although TAA ions are strongly hydrophobic. Komiyama et al. [7] have investigated the interaction between polyion and TAA ions by dilatometry. The interaction between polyion and TAA ions was discussed in detail by Zana et al. [8]. They measured the ultrasonic absorption in solutions of polyelectrolytes which are neutralized to different extents by tetraalkylammonium hydroxide and concluded that a negligible volume change is associated with the

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interaction between polyion and tetramethylammonium (TMA) ions. For this reason, in most works on the interaction between polyion and counterions [8–14], the TMA ion has been used as a reference ion. In a few papers, however, the tetra(*n*-butyl) (TBA) ion has also been used [3,15,16].

In a previous paper, we used TBA ion as a reference ion in order to discuss the interaction between polyacrylate ion and alkali metal ions. The purpose of the present work was to determine the fraction of counterions immersed in the hydration layer around a polyion as a function of the degree of neutralization by means of precise sound velocity measurement. In addition, the interaction between polyion and TAA ions will be discussed on the basis of sound velocity measurements of polyacrylate solutions neutralized by tetraalkylammonium hydroxide yielding TAA ions of different size.

2. Experimental

2.1. Samples

TAA salts of polyacrylate were prepared by neutralization of poly(acrylic acid) with the tetraalkylammonium hydroxides, $(n\text{-}C_4H_9)_4NOH$ (TBAOH), $(C_2H_5)_4NOH$ (TEAOH) and $(CH_3)_4NOH$ (TMAOH). These reagents were of guaranteed reagent grade and were used without further purification. The sample of poly(acrylic acid) was the same as that used previously [3].

2.2. Sound velocity and adiabatic compressibility

A differential type sing-around velocimeter was used to measure the sound velocity at 25.00 ± 0.001° C and a detailed description of the experimental procedure was presented previously [3]. All measurements were carried out more than twice for each sample solution.

The adiabatic compressibility in solution, β (bar^{-1}), can be determined from the sound velocity, V (m s^{-1}), and density, d (g ml^{-1}),

$$\beta = 100/V^2 d \qquad (1)$$

The solution density was measured at 25.00 ± 0.001° C, using a type DMA-02C digital precision density meter manufactured by Anton Paar Co.

3. Results

Fig. 1 shows the change in adiabatic compressibility observed when aqueous solutions of TAA salts of polyacrylate are titrated with a concentrated solution of NaCl. $\Delta\beta$ is defined as

$$\Delta\beta = \beta_s - \beta_0 \qquad (2)$$

where β_s and β_0 are the adiabatic compressibilities in solution in the presence and absence of NaCl, respectively. If the plot of $\Delta\beta$ vs. C_{NaCl}, where C_{NaCl} is the concentration of added NaCl, is linear, the decrease in $\Delta\beta$ is ascribed to the increase of NaCl in solution, as is observed for addition of NaCl to pure water. As shown in fig.

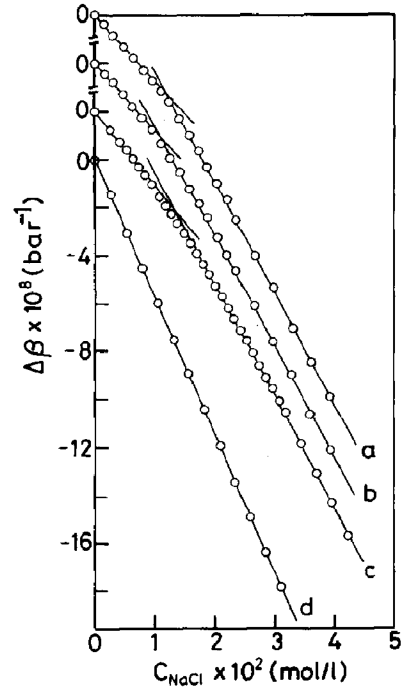

Fig. 1. NaCl concentration dependence of the adiabatic compressibility of polyacrylate solutions neutralized by TBAOH (a), TEAOH (b) and TMAOH (c) (polyacrylate concentration, 0.04 mol/l). (d) NaCl solution without polyacrylate.

1, a change in slope of the plot of $\Delta\beta$ vs. C_{NaCl} is observed for polyacrylate solutions neutralized by TMAOH, TEAOH and TBAOH. In the case of the last sample, the same behavior for $\Delta\beta$ was observed in a previous paper [3]. These changes in slope indicate that a strong interaction exists between polyacrylate ion and Na^+ due to the changes in hydration volume around the ions.

Figs. 2 and 3 show the NaCl concentration dependence of $\Delta\beta$ in polyacrylate solutions of varying degrees of neutralization, α. A change in slope of the $\Delta\beta$ vs. C_{NaCl} plot is clearly observed down to $\alpha = 0.8$. A slight deviation from linearity between $\Delta\beta$ and C_{NaCl} is evident for polyacrylate solution with $\alpha = 0.6$, while below $\alpha = 0.4$, $\Delta\beta$ changes linearly with C_{NaCl} within experimental error.

The fraction of counterions bound to polyion accompanying changes in the hydration volume around ions can be estimated from the break points in figs. 1–3, as has been done previously [3] and the results are summarized in table 1. Hereafter, the fraction of counterions bound to polyion defined above is termed as the degree of ion binding. The degree of ion binding is independent of the size of TAA ions. Although the values for the low degree of neutralization ($\alpha = 0.6$) are less reliable, it is clear that the degree of ion binding decreases with degree of neutralization. This trend has also been found using other techniques, such as measurement of transference [17], diffusion [17] and refractive index [15], but the

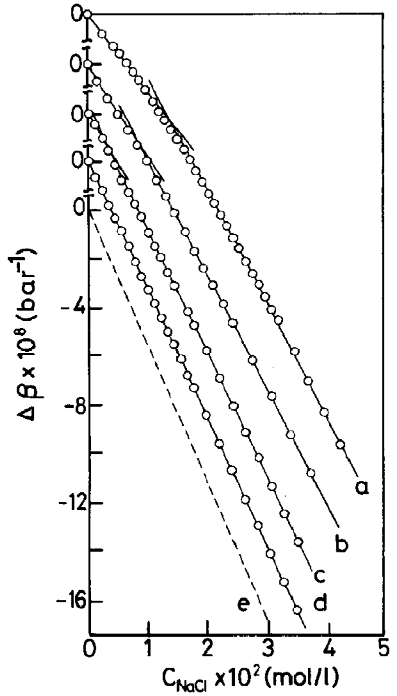

Fig. 2. NaCl concentration dependence of the adiabatic compressibility of TMA/polyacrylate solutions of different degrees of neutralization. (a) 1.0, (b) 0.8, (c) 0.6 and (d) 0.4 (concentration of -COO$^-$ group in polyacrylate solution, 0.04 mol/l). (e) NaCl solution without polyacrylate.

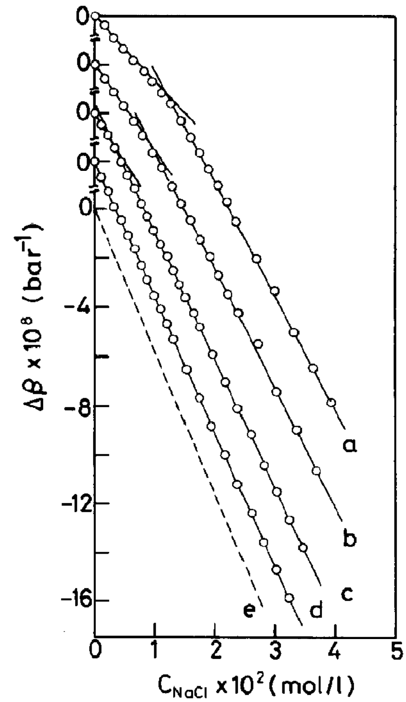

Fig. 3. NaCl concentration dependence of the adiabatic compressibility of TBA/polyacrylate solutions of different degrees of neutralization. (a) 1.0, (b) 0.8, (c) 0.6 and (d) 0.4 (concentration of -COO$^-$ group in polyacrylate solution, 0.04 mol/l). (e) NaCl solution without polyacrylate.

Table 1

Degree of ion binding (%)

α	TMA	TEA	TBA
1.0	36 ± 5	30 ± 5	30 ± 5
0.8	21 ± 5		23 ± 5
0.6	11 ± 5		10 ± 5

values for the degrees of ion binding obtained thus are larger than that estimated in this work.

The change in dehydration volume accompanying ion binding is estimated as follows [3]. The apparent molar adiabatic compressibility of NaCl in polyacrylate solution, $\phi_{\beta x}$, considering polyacrylate solution as a solvent, may be calculated from the following equation.

$$\phi_{\beta x} = 1000(\beta_s - \beta_0)/C_s + \beta_0 V_s \qquad (3)$$

where V_s is the apparent molar volume of added salt in polyacrylate solution and C_s the solute concentration. Figs. 4–6 show plots of $\phi_{\beta x}$ vs. C_{NaCl}. If it is assumed that added cations are all bound to polyion at low salt concentration, $\phi_{\beta x}$ at the limit of $C_{NaCl} = 0$ gives the molar adiabatic compressibility of NaCl for the binding state in polyacrylate solution, $\phi^b_{\beta x}$. The values of the partial molar adiabatic compressibility of NaCl in polyacrylate solutions are summarized in table 2.

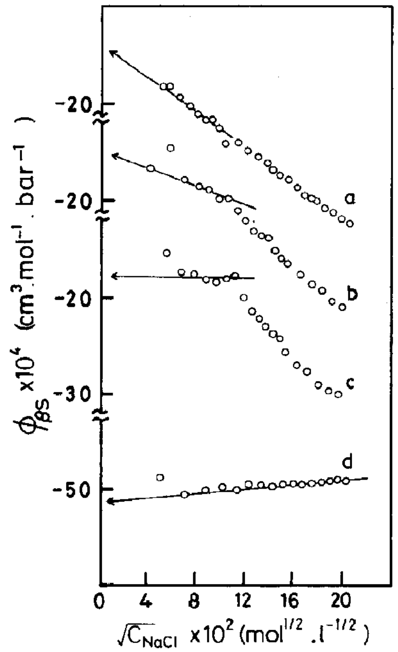

Fig. 4. Concentration dependence of the apparent molar adiabatic compressibility in polyacrylate solutions neutralized by TMAOH (a), TEAOH (b) and TBAOH (c) (polyacrylate concentration, 0.04 mol/l). (d) NaCl solution without polyacrylate.

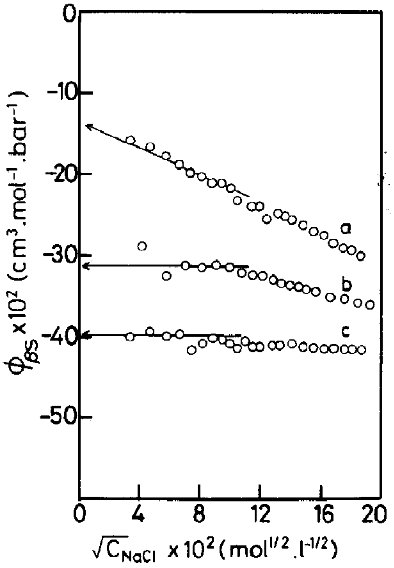

Fig. 5. Concentration dependence of the apparent molar adiabatic compressibility in TMA/polyacrylate solutions of different degrees of neutralization. (a) 1.0, (b) 0.8, (c) 0.6 and (d) 0.4 (concentration of -COO$^-$ group in polyacrylate solution, 0.04 mol/l). (e) NaCl solution without polyacrylate.

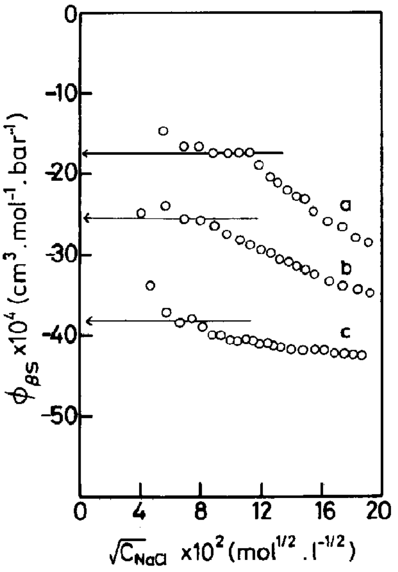

Fig. 6. Concentration dependence of the apparent molar adiabatic compressibility in TBA/polyacrylate solutions of different degrees of neutralization. (a) 1.0, (b) 0.8, (c) 0.6 and (d) 0.4 (concentration of -COO$^-$ group in polyacrylate solution, 0.04 mol/l). (e) NaCl solution without polyacrylate.

Table 2

Partial molar adiabatic compressibility of NaCl in polyacrylate solutions, $\phi_{\beta s}$ ($\times 10^{-4}$) (cm^3 mol^{-1} bar^{-1})

α	TMA	TEA	TBA
1.0	-13 ± 5	-15 ± 5	-18 ± 5
0.8	-31 ± 4		-25 ± 4
0.6	-40 ± 3		-38 ± 3

Table 3

Change in partial molar adiabatic compressibility of NaCl in polyacrylate solutions, $\Delta\phi_{\beta s}$ ($\times 10^{-4}$) (cm^3 mol^{-1} bar^{-1}) and the number of water molecules released, n_h

$\phi_{\beta s}$ of NaCl in water $= -50.8\times10^{-4}$ cm^3 mol^{-1} bar^{-1}.

α	TMA		TEA		TBA	
	$\Delta\phi_{\beta s}$	n_h	$\Delta\phi_{\beta s}$	n_h	$\Delta\phi_{\beta s}$	n_h
1.0	-38	4.7	-36	4.3	-33	4.1
0.8	-20	2.4			-26	3.2
0.6	-11	1.3			-13	1.6

If $\phi^{f}_{\beta x}$ denotes the partial molar adiabatic volume of NaCl in aqueous solution without polyacrylate, the number of water molecules released is calculated from the difference between $\phi^{b}_{\beta x}$ and $\phi^{f}_{\beta x}$, i.e., $\Delta\phi$ $(=\phi^{f}_{\beta x}-\phi^{b}_{\beta x})$ by using the relation, $\phi_{\beta x} = -n_h\beta_{H_2O}V_{H_2O}$, where β_{H_2O} and V_{H_2O} are the adiabatic compressibility and partial molar volume of pure water, respectively. Thus, the results obtained are summarized in table 3. The number of water molecules released decreases with the degree of neutralization.

Discussion

4.1. The size effect of TAA on the interaction with polyion

It is confirmed that the sound velocity or the adiabatic compressibility can reflect the interaction accompanying the changes in hydration volume. Tables 1–3 show that the degree of ion binding and the extent of the changes in hydration volume are not affected by the size of the TAA ion. This indicates that differences in size of TAA ions may have negligible influence on the interaction with polyion.

Fig. 7 shows a plot of the increase in sound velocity, ΔV, in TBA/polyacrylate solution vs. concentration of TMACl, where ΔV represents the difference in sound velocities in the presence and absence of TBA/polyacrylate. The increase in sound velocity in aqueous solutions of TMACl and TBACl is also shown in fig. 7. The sound velocity in aqueous solutions of TBACl increases sharply with concentration as compared with that of TMACl. If the interaction between polyion and TBA ion accompanies the changes in the hydration volumes around the polyion and TBA ion, the increase in sound velocity in polyacrylate solution should not vary linearly with salt concentration. As shown in fig. 7, the value of ΔV is almost linear with respect to the concentration of TMACl and the slope for the TBA/polyacrylate solution agrees with that for aqueous solution without polyelectrolyte. This result indicates that the volume change is negligible in the case of substitution of TBA by TMA ions. Therefore, we can conclude that the volume changes due to interac-

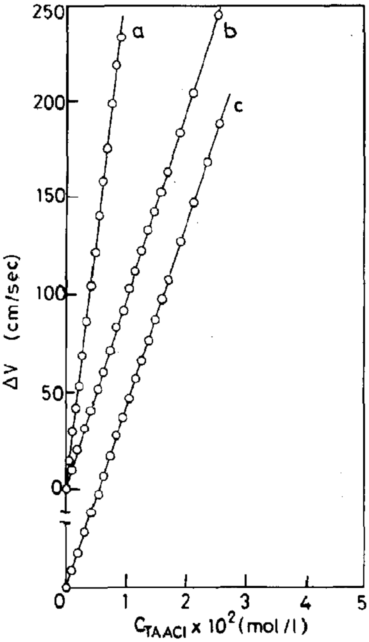

Fig. 7. TAACl concentration dependence of the increase in sound velocity, ΔV, in aqueous solution. TBACl (a) and TMACl (b) added to water. (c) TMACl added to aqueous solution of 0.04 mol/l TBA/polyacrylate.

tion of the large TAA ion with polyion and due to the rearrangement of water molecules around the polyion and TAA ion are negligible within experimental error.

However, more detailed inspection shows a slight difference between TAA ions in the concentration dependence of the apparent molar adiabatic compressibility (for example, see fig. 4). At this stage, further quantitative discussion of the slight difference observed among TAA ions is difficult owing to the accuracy in determination of the concentration of NaCl by the titration method.

4.2. Effect of charge density on the degree of ion binding

The charge density is an important factor in characterizing the properties of polyelectrolytes and can be controlled by altering the degree of neutralization, α. The degree of ion binding has been investigated from experiments and theoretical aspects as a function of degree of neutralization. As shown in table 1, the degree of ion binding decreases as the degree of neutralization, α, decreases. As the charge density in a polymer chain decreases, the hydration layer around the polyion decreases with degree of neutralization, as expected from the decrease in the electrostrictive effect of the polyion. Therefore, the overlapping region in hydration layers of polyion and counterions decreases and consequently, $\Delta\phi$ and the number of the water molecules released decrease with degree of neutralization, as shown in tables 2 and 3.

The ion binding accompanying the change in hydration volume occurs beyond about $\alpha = 0.6$. This value is greater than those reported from other experiments ($\alpha = 0$–0.3) [3,5,17]. Judging from the facts mentioned above, we can describe schematically the behaviour of counterions near polyions as follows. Below $\alpha = 0.3$, the charge density of a polyelectrolyte is so low that no ion binding occurs and the counterions behave as if they were in simple electrolyte solutions. In the intermediate region, $\alpha = 0.3$–0.6, the charge density of the polyion becomes high and ionic atmospheric interaction between the polyion and counterions occurs. Above $\alpha = 0.6$, as the charge density of the polyion increases, the hydration layer around the polyion, due to the electrostrictive effect of neighboring -COO^- groups, grows to overlap between the polyion and counterions, and the change in the hydration volume becomes detectable using sound velocity measurement.

The region of volume changes detectable also depends on the molecular structure of the polyelectrolyte, i.e., the charge spacing, hydrophobicity, etc. It is noted that the degree of ion binding and the extent of the change in volume should depend on the observable region, i.e., the experimental method.

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