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ORIGINAL CONTRIBUTION

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Thermodynamic properties of dilution of chondroitin 4-sulfate having tetraalkylammonium counterions

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Abstract The dilution enthalpies, $\Delta_{\mathrm{dil}}H$, of tetraalkylammonium chondroitin 4-sulfate (R_4NChSA) and polyacrylate (R_4NPAA) having methyl (Me), ethyl (Et), propyl (Pr) and butyl (Bu) as alkyl groups (R) were measured to elucidate the effects of hydrophobic counterions. The $\Delta_{\mathrm{dil}}H$ of R_4NChS-A and R_4NPAA were negative (exothermic) and decreased as the carbon number of tetraalkylammonium cation (R_4N^+) increased. These results were found to possess the same effects on $\Delta_{\mathrm{dil}}H$ as these of bromides. The non-electrostatic terms of dilution enthalpies $\Delta_{\mathrm{dil}}H^n$ of R_4NChS and R_4NPAA were evaluated by using the electrostatic terms of $\Delta_{\mathrm{dil}}H$ obtained from Manning's theory. The $\Delta_{\mathrm{dil}}H^n$ of R_4NChS-A and R_4NPAA decreased, i.e., their exothermic tendencies increased as the carbon number of R_4N^+ increased, and the rate of decrease of the R_4NPAA was more than that of the R_4NChS-A. These results are discussed in relation to the increase of the hydrated water structure around R_4N^+ on dilution.

Key words Chondroitin sulfate – tetraalkylammonium counterion – dilution enthalpy – thermodynamic properties – polyacrylate

Introduction

Chondroitin sulfates (ChS) are typical of glycosaminoglucans, which are known to be the important components of mammalian connective tissues, and whose function has been investigated from the biological view point. We have so far investigated the physico–chemical properties of aqueous salt-free Chs solutions. The counterion binding properties were studied by measuring osmotic coefficients, activity coefficients and partial molar volumes [1–3]. The effects of the alternate arrangements of carboxylic and sulfuric groups on the counterion bindings were analyzed using Manning's line charge theory [4], and were found to function to keep Ca^{2+} ion activity constant [2]. Furthermore, from the studies of dilution Gibbs energies, enthalpies and entropies of sodium chondroitin sulfate (NaChS) [5, 6], it was found that the amount of the non-electrostatic factor due to the polymer chain itself could not be neglected.

The significance of hydrophobic hydration and interaction have usually been studied by using tetraalkylammonium salts [7]. The effects of hydrophobic counterions of polyelectrolytes were studied by measuring osmotic coefficients and mean activity coefficients of polyacrylates having R_4N^+, and the R_4NPAA were found to increase with the chain length of R_4N^+ [8, 9]. These increases were attributed to the ability of R_4N^+ to form an iceberg around itself in water.

The polymer ChS is hydrophilic because of the presence of sugar rings and dissociable groups. However, using the R_4N^+ as counterions of ChS, the R_4NChS becomes partly hydrophobic and soluble in some organic solvents. The effects of the R_4N^+ on interfacial adsorption of R_4NChS were significant, and the effects of arrangements of counterions along ChS chains were found to enhance the interfacial adsorptions of the chains, especially when the carbon number of R was greater than 2 [10]. Their transfer molar enthalpies from water to urea solutions depended significantly on the properties of R_4N^+, and were found to be almost the same as those of R_4NBr [11]. In this report, the effects of hydrophobic counterions on the thermodynamic properties of ChS were studied in the manner described in our preceding paper, using vapor pressure osmometry and calorimetry [6].

Materials and methods

Materials

Sodium chondroitin 4-sulfate (NaChS-A) was of commercial origin (super special grade, Seikagaku Kogyo Co., Ltd., Tokyo, Japan), and was extracted from whale cartilage. Its average molecular weight was determined by viscosity measurement to be 2.0×10^4 [12].

Ammonium and tetraalkylammonium chondroitin 4-sulfates (NH_4ChS-A and R_4NChS-A) with methyl (Me), ethyl (Et), propyl (Pr) and butyl (Bu) as alkyl groups (R) were prepared by the following two procedures [10]. Procedure I: NH_4ChS-A and Me_4NChS-A were obtained by passing NaChS-A through columns of cation exchange resins (Amberlite IR-120B), which were previously converted into the corresponding counterion forms. Procedure II: Tetraethylammonium, tetrapropylammonium and tetrabutylammonium ChS-A salts (Et_4N-, Pr_4N- and Bu_4NChS-A) were prepared by neutralizing chondroitin sulfuric acid (HChS-A) with the corresponding tetraalkylammonium hydroxides. HChS-A was obtained from NaChS-A by passing it through the cation exchange column treated previously with acid. Because of the tendency of ChS in the acidic pH region (pH < 2) to hydrolyze the sulfate group and to degrade the polymer chain, the treatment of HChS-A was carried out as quickly as possible. Since the reduced viscosities of NaChS-A reconstituted by Procedure II were not different from those of the original NaChS-A, ChS-A salts obtained by Procedure II were regarded not to be degraded. Furthermore, the completeness of the counterion exchanges was verified by the negligible concentrations of residual Na^+ ions that were analyzed by Atomic Spectrophotometer (SEIKO, SAS-710). The ChS-A salts thus obtained in aqueous solutions were freeze-dried *in vacuo*.

Sodium polyacrylate (NaPAA) was provided by Toa Gosei Chemical Co., Ltd., Nagoya, Japan. Its average molecular weight was determined by viscosity measurement to be about 1.4×10^5 [13]. Tetraalkylammonium polyacrylates (R_4NPAA) were obtained by neutralizing polyacrylic acid with corresponding tetraaklylammonium hydroxides and then performing dialysis.

Tetraalkylammonium hydroxides (special grade, 10% in water) were obtained from Tokyo Kasei Co., Ltd., Tokyo, Japan, and other electrolytes were obtained from Katayama Kagaku Co., Ltd., Osaka, Japan. Distilled and deionized water was used for the preparation of the sample solution.

Method

(1) *Enthalpies of dilution* ($\Delta_{\text{dil}}H$): The dilution enthalpies of ChS, $\Delta_{\text{dil}}H$, were each obtained as the heat arising from the mixing of ChS aq. solution (initial concentration, m_i; final concentration, m_f) with water in a twin-type conduction micro calorimeter (CM204 D1; Rhesca Co., Ltd, Japan). The measured values were converted into values corresponding to one mole of the ChS repeating unit. The detailed procedure for calorimetry was as previously reported [5, 14]. An isoperibol solution calorimeter (Calorimetry Sciences Co., Ltd., Utah, U.S.A.) was also used to confirm the dilution enthalpy of Bu_4NPAA in an aqueous solution. Isoperibol solution calorimetry is a technique in which the temperature of a reaction vessel in a constant-temperature environment is monitored as a function of time. The isoperibol solution calorimeter includes a Dewar vessels as the reaction cell, a rapid responding thermistor as the temperature-measuring device, and an electrical heater for temperature equilibration and calibration. This calorimeter measures the heat produced when two solutions are mixed. The temperature change, caused by any reaction occurring as the solutions are mixed, is detected by the temperature sensor and converted by the electronic output circuit to a signal corresponding to the temperature change.

(2) *Osmotic coefficient* (ϕ): Osmotic coefficients, ϕ, [15] were measured by means of vapor-pressure osmometry using the Hitachi–Perkin–Elmer Model 115 Molecular Weight Apparatus described previously [1]. Aqueous NaCl solutions having an osmotic coefficient, ϕ', were used as reference solution. Under the isopiestic condition between the reference NaCl solution and a polyelectrolyte solution, the osmotic coefficient of polyelectrolyte, ϕ, is given by

$$\phi = \frac{2m'\phi'}{(z/z_g + 1)(2m/z_r)}, \tag{1}$$

where m and m' are the molality of ChS on a repeating unit basis and that of NaCl, ϕ' is the osmotic coefficient of NaCl (obtainable from the literature), and z, z_g and z_r are the stoichiometric charges per polymer, counter ion and repeating unit, respectively.

Results

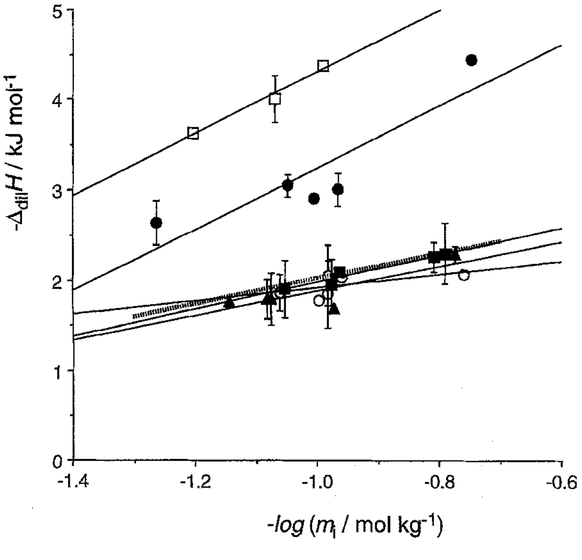
Dilution enthalpies of R_4NChS-A and R_4NPAA salts

The dilution enthalpies, $\Delta_{dil}H$, of R_4NChS-A, from various initial concentrations m_i to the final concentration $m_f (= 3.85 \times 10^{-3}$ mol kg$^{-1})$ at 298.15 K are shown in Fig. 1. These enthalpies were negative – that is, exothermic – and were found to decrease as both m_i and the carbon number of R_4N^+ counterion increased. The values from $m_i = 0.1$ to $m_f = 3.85 \times 10^{-3}$ mol kg^{-1} are plotted against temperatures in Fig. 2. They had a general tendency to increase slightly with temperature.

Figure 3 shows the dilution enthalpies of R_4NPAA from various m_i to $m_f = 3.85 \times 10^{-3}$ mol kg^{-1} at 298.15 K. These conditions were the same as those of R_4NChS-A shown in Fig. 1. The $\Delta_{dil}H$ for R_4NPAA were also exothermic and decreased with the carbon number of R_4N^+.

Figure 4 shows the $\Delta_{dil}H$ of R_4NChS-A and -PAA diluted from $m_i = 0.1$ to $m_f = 3.85 \times 10^{-3}$ mol kg^{-1} as a function of the carbon number N of hydrocarbon R at 298.15 K. As ChS salts possess two R_4N^+ counterions in one repeating unit, the values converted to 1 mole bases of R_4N^+ counterions are shown with closed circles in Fig. 4. The values for tetraalkylammonium and sodium bromides (R_4NBr and NaBr) diluted in the same range are also shown in Fig. 4. They were obtained from the relative apparent molal enthalpies. ϕ_L, referred to data of Lindenbaum [16], and Harned and Owen [17], according to the

Fig. 1 Dilution enthalpies of R_4NChS-A diluted from various initial concentrations m_i to the final concentration $m_f = 3.85 \times 10^{-3}$ mol kg^{-1} at 298.15 K, ▲: NaChS-A, ○: Me_4NChS-A, ■: Et_4NChS-A, ●: Pr_4NChS-A, □: Bu_4NChS-A. The dotted line represents the theoretical values of Manning's limiting law obtained by using $b = 0.48$ nm as the distance between the neighboring charges of ChS-A. Vertical bars denote S.D



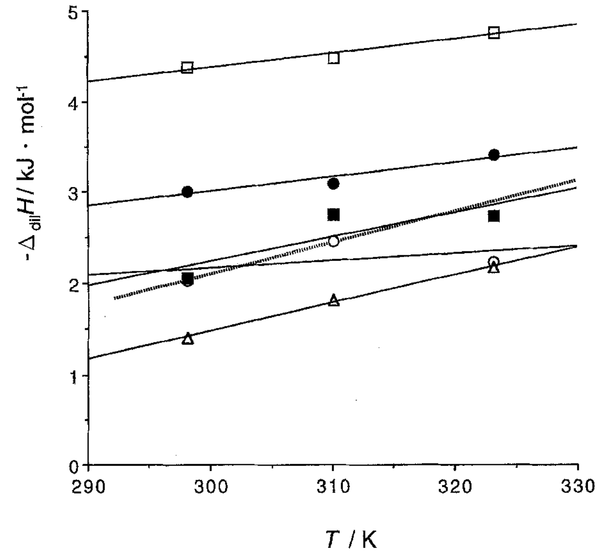


Fig. 2 Effect of temperatures on dilution enthalpies of R_4NChS-A diluted from the initial concentration $m_i = 0.1$ to the final concentration $m_f = 3.85 \times 10^{-3}$ mol kg^{-1}, △: NH_4ChS-A. Other symbols are the same as in Fig. 1

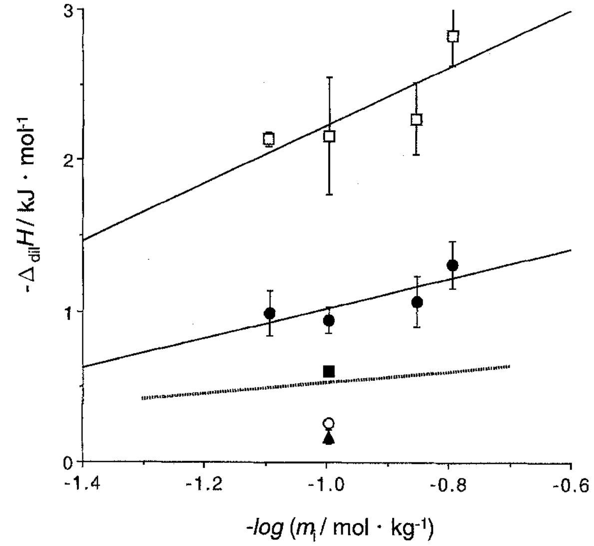


Fig. 3 Dilution enthalpies of R_4NPAA and NaPAA diluted from the initial concentration m_i to the final concentration $m_f = 3.85 \times 10^{-3}$ mol kg^{-1} at 298.15 K, ▲: NaPAA, ○: Me_4NPAA, ■: Et_4NPAA, ●: Pr_4NPAA, □: Bu_4NPAA. The dotted line represents the theoretical values of Manning's limiting law obtained by using $b = 0.25$ nm as the distance between the neighboring charges of PAA. Vertical bars denote S.D

following equation,

$$\Delta_{\mathrm{dil}}H = \phi_{\mathrm{L}}(m_{\mathrm{f}}) - \phi_{\mathrm{L}}(m_{\mathrm{i}}) \; . \qquad (2)$$

As the concentration of m_f was relatively low, the $\phi_L(m_f)$ of R_4NBr were assumed to be equal to that of NaBr ($\phi_L(m_f) = 103\ \mathrm{J\,mol^{-1}}$). The values of R_4NChS-A were 1.3–1.8 kJ mol^{-1} less than those of R_4NBr except for the case of NaChS-A which was 0.7 kJ mol^{-1} less than NaBr, but it can be said that the variation of their $\Delta_{\mathrm{dil}}H$ with the carbon number was in good agreement. On the other hand, the $\Delta_{\mathrm{dil}}H$ of R_4NPAA were near to those of R_4NBr when N was less than 2, but with increases of N the values approached those of R_4NChS-A. Overall, it should be said that the $\Delta_{\mathrm{dil}}H$ of R_4N salts decreased with increasing N. These results suggest that the R_4N^+ counterions of these polyelectrolytes and bromides have the same effects on the dilution enthalpies. This argument is strengthened by our earlier results [11], which showed that the transfer enthalpies of R_4NChS-A from water to urea varied with the carbon number of R in the same manner as those of R_4NBr. The difference between ChS salts and bromides suggests the presence of polymer effects resulting from the arrangements of R_4N^+ counterions on the polymer chains, which depend on the distance between the neighboring charge groups and the length of the chains.

The thermodynamic properties seen during the dilution of tetraalkylammonium halides, R_4N-X, have been studied to elucidate the interaction between H_2O and hydrocarbons. Lindenbaum reported that the heat evolved in the dilution of tetraalkylammonium halides increased with the carbon number in the following order, $(C_4H_9)_4N_- > (C_3H_7)_4N_- > (C_2H_5)_4N_- > (CH_3)_4N_-$ [16]. This may be explained as followings: the amount of the hydrated water structure around the hydrocarbons tends to increase with the carbon number, and the increase of this structure in the dilution process results in evolving heat because it decreases the overlap of the hydration domain. The concentration ranges of R_4N–X reported by Lindenbaum were higher than those of the polymer samples used in this report. However, the local concentration of R_4N^+ counterions of polymers is considered to be enough for R_4N^+ ions to interact with each other. The water structure around R_4N^+ ions may overlap at the initial concentration, $m_i = 0.1\ \mathrm{mol\,kg^{-1}}$, through inter- and intrachain interaction, and the overlap of the hydration domain decreases on dilution. In this way, the exothermic tendencies of the dilution enthalpies of R_4NChS and R_4NPAA can be explained in the same manner as that of R_4NBr.

Thermodynamic quantities of dilution of R_4NChS-A

The osmotic coefficients, ϕ, of R_4NChS-A at 310.15 K are shown in Fig. 5. The values of ϕ in the experimental ranges are linear functions of the concentration, m, as in the case of alkali metal ChS salts [1]. The ϕ values of R_4NChS-A increased with m. They also show that the ϕ values

Fig. 4 Effect of carbon number of R_4N^+ counterions N on dilution enthalpies of ChS-A, PAA and bromides at 298.15 K, ○: R_4NChS-A, ●: R_4NChS-A (based on 1 mole R_4N^+ counterion), □: R4NPAA, △: R4NBr. The solutes of $N = 0$ are Na salts

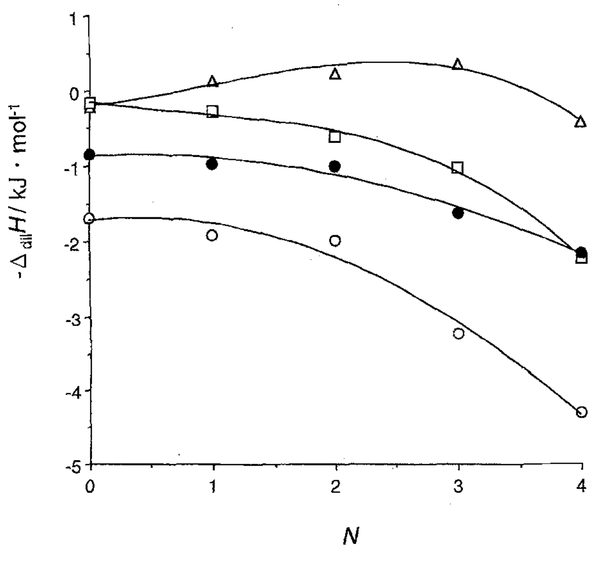
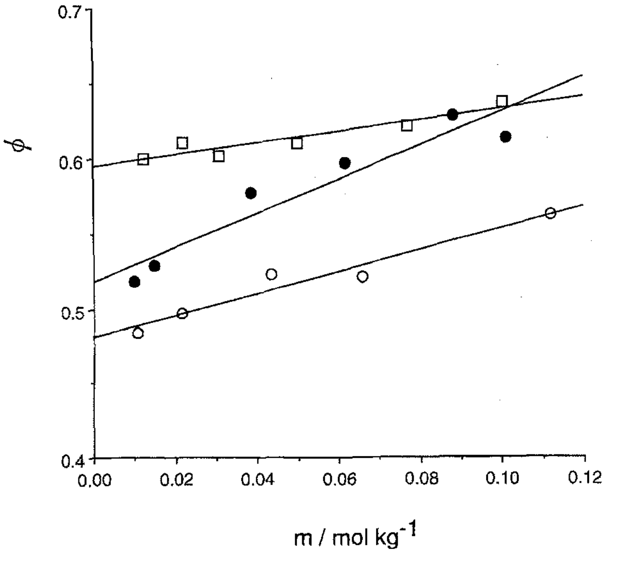


Fig. 5 Concentration dependencies of osmotic coefficients of R_4NChS-A at 310.15 K, ○: Me_4NChS-A, ●: Pr_4NChS-A, □: Bu_4NChS-A



increased with the carbon number in the following order, $Me_4N^+ < Pr_4N^+ < Bu_4N^+$. As our earlier paper showed [16], the Gibbs energy of dilution, $\Delta_{\mathrm{dil}}G$, can be calculated from the osmotic coefficient, ϕ, by using graphic integration according to the following equations.

$$\Delta_{\mathrm{dil}}G = 2(1/z + 1/z_g)\, RT \ln\left(\frac{m_f \gamma_{\pm,f}}{m_i \gamma_{\pm,i}}\right) \quad (3)$$

$$\ln(\gamma_{\pm}/\gamma_i) = (\phi_f - \phi_i) + 2\int_{m_f}^{m_i} \frac{1-\phi}{\sqrt{m}}\, d\sqrt{m}\,, \quad (4)$$

where $\gamma_{\pm}$ is the mean activity coefficient of ChS salts and subscripts i and f represent the initial and final concentrations. From the values of $\Delta_{\mathrm{dil}}G$ and $\Delta_{\mathrm{dil}}H$, the dilution entropies, $\Delta_{\mathrm{dil}}S$, can be obtained by the thermodynamic relation, $\Delta_{\mathrm{dil}}S = (\Delta_{\mathrm{dil}}H - \Delta_{\mathrm{dil}}G)/T$. The temperature dependence of $\Delta_{\mathrm{dil}}H$ is the change of the apparent molal heat capacity, $\Delta_{\mathrm{dil}}Cp$, as expressed by the following equation,

$$(\delta\Delta_{\mathrm{dil}}H/\delta T)_p = \Delta_{\mathrm{dil}}Cp\,. \quad (5)$$

The thermodynamic parameters obtained for R_4N_- and NaChS-A salts diluted from $m_i = 0.1$ to $m_f = 3.85 \times 10^{-3}$ $\mathrm{mol\,kg^{-1}}$ at 310.15 K, are summarized in Table 1. $\Delta_{\mathrm{dil}}G$ decreased as the carbon number and $\Delta_{\mathrm{dil}}H$ increased. On the other hand, the change of $\Delta_{\mathrm{dil}}S$ is found to reach the maximum value of in Pr_4NChS. The calculated accuracy of $\Delta_{\mathrm{dil}}S$ is governed by the experimental error of $\Delta_{\mathrm{dil}}H$ rather than the calculated $\Delta_{\mathrm{dil}}G$ from Eqs. (3) and (4). It can be presumed that the calculated error of $\Delta_{\mathrm{dil}}S$ is about $\pm 0.8\ \mathrm{J\,mol^{-1}\,K^{-1}}$, in Table 1.

Discussion

Non-electrostatic terms in dilution process

ChS-A in dilute solution behaves as a rod-like polyelectrolyte because of the repulsive electrostatic force between the negatively charged groups of the polymer chains and because of the rigidity of their saccharide structure. The thermodynamic properties of a rod-like polyelectrolyte have been analyzed using a line charge model [4] and a cylindrical model [18–20], and the limitations of these models were discussed by comparing the theoretical results with the experimental ones [21–24]. The electrostatic contribution to the thermodynamic properties of ChS-A having metal ions as counterions were found to be explained by Manning's line charge model [1, 2, 5, 6].

The thermodynamic quantities of dilution, $\Delta_{\mathrm{dil}}Y(\Delta_{\mathrm{dil}}H, \Delta_{\mathrm{dil}}G$ and $\Delta_{\mathrm{dil}}S)$ of R_4NChS-A, can be divided into the electrostatic and the non-electrostatic terms, $\Delta_{\mathrm{dil}}Y^{\mathrm{el}}$ and $\Delta_{\mathrm{dil}}Y^{\mathrm{n}}$,

$$\Delta_{\mathrm{dil}}Y = \Delta_{\mathrm{dil}}Y^{\mathrm{el}} + \Delta_{\mathrm{dil}}Y^{\mathrm{n}}\,. \quad (6)$$

Neglecting the interaction between polyions in low concentrations, $\Delta_{\mathrm{dil}}H^{\mathrm{el}}$ and $\Delta_{\mathrm{dil}}G^{\mathrm{el}}$ are expressed by Manning's limiting law:

$$\Delta_{\mathrm{dil}}H^{\mathrm{el}} = (RT/\xi)\,(1 + (T/\varepsilon)\,(d\varepsilon/dT))\ln(m_i/m_f), \quad \xi \geq 1 \quad (7)$$

$$\Delta_{\mathrm{dil}}G^{\mathrm{el}} = -(RT/\xi)\ln(m_i/m_f), \quad \xi \geq 1\,, \quad (8)$$

where ε is the permittivity of the solvent (water), and ξ is the charge density parameter, which is defined by the following equation:

$$\xi = e^2/4\pi\varepsilon kTb\,, \quad (9)$$

where e is a protonic charge, b is the distance between the neighboring charge groups of a polyion and the other symbols have the usual meanings. For NaChS-A, $b = 4.8$ Å, which was obtained from the x-ray diffraction of NaChS film [25, 26], was selected so as to fit the theoretical values, $\Delta_{\mathrm{dil}}H^{\mathrm{el}}$, to the experimental ones by assuming $\Delta_{\mathrm{dil}}H^{\mathrm{n}} = 0$ [5, 6]. The values of $\Delta_{\mathrm{dil}}H^{\mathrm{el}}$ thus obtained are shown as a dotted line in Fig. 1 as a function of $-\log m$, and in Fig. 2 as a function

Table 1 Thermodynamic quantities of dilution of R_4NChS-A and NaChS-A at 310.15 K[a)]

	$\Delta_{\mathrm{dil}}Y^{\mathrm{el}}$	Na^-	Me_4N^-	Pr_4N^-	Bu_4N^-
$\Delta_{\mathrm{dil}}H/\mathrm{kJ\,mol^{-1}}$	−2.44	−2.59	−2.46	−3.10	−4.48
$\Delta_{\mathrm{dil}}G/\mathrm{kJ\,mol^{-1}}$	−5.60	−8.80	−8.83	−9.99	−10.53
$\Delta_{\mathrm{dil}}S/\mathrm{J\,mol^{-1}\,K^{-1}}$	10.1	20.0	20.5	22.2	19.5
$\Delta_{\mathrm{dil}}C_p/\mathrm{J\,mol^{-1}\,K^{-1}}$	35.2			−20.0	−15.0
$\Delta_{\mathrm{dil}}H^{\mathrm{n}}/\mathrm{kJ\,mol^{-1}}$		−0.15	−0.02	−0.66	−2.04
$\Delta_{\mathrm{dil}}H^{\mathrm{n}}/\mathrm{kJ\,mol^{-1}}$ (R_4N^-)		−0.08	−0.01	−0.33	−1.02
$\Delta_{\mathrm{dil}}G^{\mathrm{n}}/\mathrm{kJ\,mol^{-1}}$		−3.20	−3.23	−4.39	−4.93
$\Delta_{\mathrm{dil}}S^{\mathrm{n}}/\mathrm{J\,mol^{-1}\,K^{-1}}$		9.9	10.4	12.1	9.4
$\Delta_{\mathrm{dil}}H^{\mathrm{R}}/\mathrm{kJ\,mol^{-1}}$		0	0.13	−0.51	−1.890
$\Delta_{\mathrm{dil}}H^{\mathrm{R}}/\mathrm{kJ\,mol^{-1}}$ (R_4N^-)		0	0.065	−0.26	−0.945
$\Delta_{\mathrm{dil}}G^{\mathrm{R}}/\mathrm{kJ\,mol^{-1}}$		0	−0.03	−1.19	−1.73
$\Delta_{\mathrm{dil}}S^{\mathrm{R}}/\mathrm{J\,mol^{-1}\,K^{-1}}$		0	0.5	2.2	−0.5

[a)] Dilution range: from $m_i = 0.1$ to $m_f = 3.85 \times 10^{-3}$ mol/kg.

of temperature. The deviations of the $\Delta_{\text{dil}}H$ of R_4NChS-A from Manning's $\Delta_{\text{dil}}H^{\text{el}}$ can be ascribed to the non-electrostatic term. $\Delta_{\text{dil}}H^{\text{n}}$, which results primarily from the enhancement of the water structure around R_4N^+ counterion on dilution. Figure 6(a) shows the $\Delta_{\text{dil}}H^{\text{n}}$ of R_4NChS-A at 298.15 K, which are converted to 1 mole bases of R_4N^+ for comparison with the results of R_4NPAA. The values of $\Delta_{\text{dil}}H^{\text{n}}$ decreased with the carbon number of R_4N^+.

For PAA salts, we adopted 2.5 Å as the b value, following Ise et al. [27] and Mita and Okubo [28]. The theoretical values of $\Delta_{\text{dil}}H^{\text{el}}$, calculated from Eqs. (7) and (9), are shown in Fig. 3 as a dotted line. The $\Delta_{\text{dil}}H$ values of NaPAA showed a positive deviation from $\Delta_{\text{dil}}H^{\text{el}}$, that is, $\Delta_{\text{dil}}H^{\text{n}} = 0.36\ \text{kJ mol}^{-1}$ at 298.15 K. The value of this non-electrostatic term depends on the structure of the polymer chain itself. As shown in Fig. 6(a), the $\Delta_{\text{dil}}H^{\text{n}}$ of R_4NPAA, as well as of R_4NChS-A, both of which consist of a contribution from the polymer chain and the R_4N^+ counterion, decreased with the carbon number.

The non-electrostatic term of thermodynamic quantities can be divided into the terms of the polymer chain itself and the counterion. Assuming that the contribution to the dilution enthalpy from the polymer chain $\Delta_{\text{dil}}H^{\text{P}}$ is a common term regardless of the counterion species, and is equal to the $\Delta_{\text{dil}}H^{\text{n}}$ of the Na salt, $\Delta_{\text{dil}}H^{\text{n}}$ can be presented by the following equation,

$$\Delta_{\text{dil}}H^{\text{n}} = \Delta_{\text{dil}}H^{\text{P}} + \Delta_{\text{dil}}H^{\text{R}}\ , \tag{10}$$

where $\Delta_{\text{dil}}H^{\text{R}}$ is the non-electrostatic term resulting from the interaction between R_4N^+ counterions. As mentioned above, the $\Delta_{\text{dil}}H^{\text{P}}$ of ChS is $0.16\ \text{kJ mol}^{-1}$ on the basis of 1 mole R_4N^+, and the $\Delta_{\text{dil}}H^{\text{P}}$ of PAA is equal to $0.36\ \text{kJ mol}^{-1}$ at 298.15 K. The $\Delta_{\text{dil}}H^{\text{R}}$ are shown in Fig. 6(b) as a function of N. The values $\Delta_{\text{dil}}H^{\text{R}}$ of R_4NChS-A and R_4NPAA decreased with increasing N, and the latter values were slightly less than the former. This may be ascribed to the smaller b values of PAA.

In Table 1, the non-electrostatic terms of Gibbs energy and entropy, $\Delta_{\text{dil}}G^{\text{n}}$, $\Delta_{\text{dil}}S^{\text{n}}$, $\Delta_{\text{dil}}G^{\text{R}}$, and $\Delta_{\text{dil}}S^{\text{R}}$ are shown together with other thermodynamic quantities of dilution at 310.15 K. $\Delta_{\text{dil}}G^{\text{n}}$ and $\Delta_{\text{dil}}H^{\text{n}}$ were negative and decreased with the carbon number of R_4N^+. On the other hand, $\Delta_{\text{dil}}S^{\text{n}}$ were found to be near $10\ \text{J mol}^{-1}\text{K}^{-1}$ and to tend to decrease the carbon numbers increased.

In addition, Ise et al. [27] previously reported for the dilution enthalpies of aqueous solutions of PAA having various counterions that the $\Delta_{\text{dil}}H$ value of the NaPAA was exothermic, whereas those of R_4N salts were endothermic. Their data are in conflict with our results. An isoperibol solution calorimeter, which is based on a different principle of calorimetric measurement, was therefore used to confirm our results, and the dilution enthalpy and the solution enthalpy, $\Delta_{\text{sol}}H$, of Bu_4NPAA in aqueous solution were measured at 298 K. As Table 2 shows, both the $\Delta_{\text{dil}}H$ value and the $\Delta_{\text{sol}}H$ value of Bu_4NPAA were exothermic, data that support our results with the twin-type calorimeter. In this regard, Daoust and Chabot [29] reported that the intermediate heat of dilution (Δh_{d}) as a function of initial molality in a 1:1 dilution was measured for Me_4NPAA. Exothermic Δh_{d} values at high concentrations and endothermic Δh_{d} values at low concentrations for aqueous solutions of Me_4NPAA. Our results are consistent with the data of Daoust and Chabot in the high concentration range of dilutions measured. To solve the inconsistencies for the report of Ise et al., it will be necessary to measure $\Delta_{\text{dil}}H$ of aqueous R_4NPAA solutions over a wide range of dilutions.

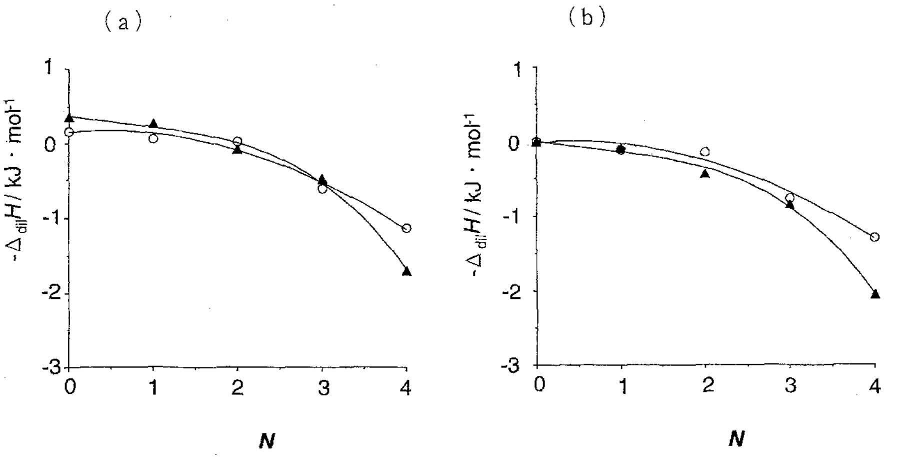


Fig. 6 Effect of carbon number of R_4N^+ counterions N on non-electrostatic terms of dilution enthalpies of ChS-A and PAA salts at 298.15 K, (a) $\Delta_{\text{dil}}H^{\text{n}}$ vs. N, (b) $\Delta_{\text{dil}}H^{\text{R}}$ vs. N, ●: R_4NChS-A (based on 1 mole R_4N^+ counterion), □: R_4NPAA. The solutes of $N = 0$ are Na salts

Table 2 Dilution enthalpy and solution enthalpy of Bu_4NPAA at 298 K by use of an isoperibol solution calorimeter

m_i/mol·kg^{-1}	m_f/mol·kg^{-1}	$\Delta_{dil}H$/kJ·mol^{-1}	$\Delta_{sol}H$/kJ·mol^{-1}
0.068	1.9×10^{-3}	-5.0	–
–	1.5×10^{-3}	–	-47.3

Conclusions

1) The $\Delta_{dil}H$ values of R_4NChS-A and R_4NPAA were negative (exothermic) and decreased as the carbon number of R_4N^+ increased. Furthermore, the non-electrostatic terms of the dilution enthalpies, $\Delta_{dil}H^n$, of R_4NChS-A and R_4NPAA decreased, i.e., the exothermic tendencies increased, as the carbon number of R_4N^+ rose, and the rate of $\Delta_{dil}H^n$ decrease of R_4NPAA was more than that of R_4NChS. This may have resulted from the smaller distance between the neighboring charge groups.

2) The R_4N^+ counterions of ChS and PAA have the same effects on $\Delta_{dil}H$ as those of the bromides. As with R_4NBr, these exothermic tendencies are believed to result from the increased amount of the hydrated water structure around R_4N^+ on dilution because of the decrease in the overlap of the hydration domain.

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