Hydration Behavior of Ionic Dextran Derivatives

Kunihiko Gekko* and Hajime Noguchi

Department of Food Science and Technology, Faculty of Agriculture, Nagoya University, Nagoya, Japan 464. *Received August 20, 1973*

ABSTRACT: The partial molal volume and the partial specific adiabatic compressibility ($\bar{\beta}^0$) were determined for sodium salts of carboxymethyldextran (CMD), sulfopropyldextran (SPD), and dextran sulfate (DS) having different degrees of substitution in aqueous solution at 25°. The hydration behavior of these derivatives was discussed in terms of three kinds of hydration: electrostricted hydration around the ionic group, hydrophobic hydration around the nonpolar group, and hydrogen-bonded hydration around the polar group. The total volume changes associated with hydration decrease linearly with increasing degree of substitution. The volume changes by electrostriction for COO^- and SO_3^- groups were estimated to be −21.2 and −30.3 ml per mol of ionic group, respectively, and the volume change by hydrophobic hydration around the propyl group of SPD was −7.5 ml/mol of propyl group. The values of $\bar{\beta}^0$ for all derivatives were negative and decreased with increasing degree of substitution and in the order SPD > DS > CMD at the same degree of substitution. The adiabatic compressibility of water of hydrophobic hydration or icebergs surrounding the propyl group appears to lie between those for ice and liquid water.

Recently the hydration behavior of polyelectrolytes has been studied quantitatively by several authors.[1-6] Conway *et al.* and Ise and Okubo have obtained some interesting information on the hydration of synthetic polyelectrolytes by estimating the amount of electrostrictional hydration and hydrophobic hydration separately.[1-5] At present, the clarification of the role and the characteristic properties of this water of hydrophobic hydration or icebergs is a matter of concern of many investigators.

More recently we studied the interaction of the ionic dextran derivatives, that is, carboxymethyldextran, sulfopropyldextran, and dextran sulfate, with alkali ions through measurements of electric conductivity, sound velocity and counterion activity coefficient and found that there exists a specific site binding between potassium ion and dextran sulfate in addition to the usual electrostatic diffuse binding.[7] On the other hand, it is necessary to examine the hydration phenomena of these macroions in order to understand their characteristic properties in the aqueous solutions. We already elucidated the hydration behavior of the dextran molecule and determined the amount of hydrogen-bonded hydration around OH groups depending on the molecular weight of dextran.[8] In that case it was not so complicated to analyze the hydration phenomena as water molecules are mainly attracted to OH groups on the glucose ring of dextran. However, if any ionic group is introduced on the dextran molecule, the elucidation of the hydration behavior of such ionic dextran derivatives becomes very difficult because it is then necessary to take account of different types of hydration, the hydrophobic hydration around the nonpolar group and the well-known electrostrictional hydration around the ionic group besides the hydrogen-bonded hydration around OH group; consequently only few quantitative investigations[6,9] have so far been reported in relation to the hydration of the ionic polysaccharides.

In this work, the partial molal volume and the partial specific adiabatic compressibility are measured for the ionic dextran derivatives in order to clarify the influence of ionic groups and their degree of substitution on the hydration behavior in the aqueous solution, which should contribute to an understanding of the characteristic properties of the ionic polysaccharides and some biochemical phenomena such as their interactions with proteins.

Experimental Section

Materials. Three kinds of dextran derivatives, dextran sulfate (DS), carboxymethyldextran (CMD), and sulfopropyldextran (SPD) having different degree of substitution, were used. These purified derivatives were almost the same materials as in the previous work,[7] which were kindly supplied by Research Institute of Meito Sangyo Co., Ltd., Nagoya. The characteristic properties of dextran derivatives used are listed in Table I. The parent dextran of these derivatives has a few branchings (96% 1,6 linkages) and a molecular weight of 50,000 which was determined by viscometry. Aqueous solutions of sodium form derivatives were passed through a mixed-bed ion-exchange resin column and the acid form polymers thus obtained were completely neutralized with sodium hydroxide in a potentiometric titration.

Sound Velocity Measurement. The sound velocity in the solution was measured by a "sing-around pulse method" of high stability and precision developed by Greenspan and Tschiegg[10] as described in previous papers.[7,8] The accuracy in measurements corresponds to a sensitivity of one part in 10^6. The solution and solvent were completely degassed under vacuum before measurements. All measurements were carried out over the concentration range of 0.002–0.01 g/ml at 25 ± 0.001°. The concentration of the solution was determined by the dry weight method after measurements of sound velocity and density.

The partial specific compressibility of solute, $\bar{\beta}^0$, is defined as follows

$$\bar{\beta}^0 = -(1/\bar{v}^0)(\partial\bar{v}^0/\partial P) = \beta_0/\bar{v}^0 \lim_{c \to 0}(\beta/\beta_0 - V_0)/c \quad (1)$$

where

$$V_0 = (d - c)/d_0 \quad (2)$$

$$\bar{v}^0 = \lim_{c \to 0}(1 - V_0)/c \quad (3)$$

The notations used are: β, adiabatic compressibility of solution; β_0, adiabatic compressibility of solvent; d, density of solution; d_0, density of solvent; c, concentration of solute, grams per milliliter of solution; V_0, apparent volume fraction of solvent in solution; $\bar{v}^0$, partial specific volume of solute. The values of β and β_0 can be calculated from the results of measurements on the sound velocity, u, and the density, d, of the solution or solvent, using the following equation

$$u^2 = 1/d\beta \quad (4)$$

Density Measurement. The densities of the solutions were determined by an ordinary Gay-Lussac-type pycnometer having a volume of about 16 ml and a capillary diameter of about 0.5 mm. The pycnometer containing the degassed aqueous solution or distilled water was immersed in a thermostat controlled at 25 ± 0.001°. After thermal equilibrium was attained, the overflowed liquid on the top of the capillary was wiped off and then the pycnometer was simultaneously taken out from the thermostat. The weight of the pycnometer was measured every 30 sec after the water on its surface was completely wiped off with a tissue containing acetone and the actual weight of the pycnometer containing the solution was determined by extrapolating the apparent values of weight to zero time, to eliminate an error due to vaporization of solvent. The density thus obtained in this experiment is

Table I
Characteristic Properties of Dextran Derivatives

Dextran Derivative	Sulfur Content (%)	Deg of Substitution	Mean Mol Wt of Deriv (Acid Form)
Sulfopropyldextran, SPD-4	6.9	0.51	6.9×10^4
Sulfopropyldextran, SPD-3	10.0	0.92	8.4×10^4
Sulfopropyldextran, SPD-2	12.3	1.41	10.3×10^4
Sulfopropyldextran, SPD-1	14.6	2.20	13.2×10^4
Dextran sulfate, DS-3	8.7	0.61	6.5×10^4
Dextran sulfate, DS-2	15.0	1.46	8.6×10^4
Dextran sulfate, DS-1	19.3	2.54	11.2×10^4
Carboxymethyldextran, CMD-2F		0.72	6.3×10^4
Carboxymethyldextran, CMD-1F		1.60	7.9×10^4

estimated to be precise within ±0.00003. The partial specific volume of each polyelectrolyte, $\bar{v}^0$, was calculated from the density data using eq 3. The partial molal volume per monomer unit of polyelectrolyte was determined by multiplying the $\bar{v}^0$ values by the molecular weight of monomer unit.

Results and Discussion

Partial Molal Volume. As seen from Figure 1, the apparent specific volume of each derivative, $(1 - V_0)/c$, is almost independent of the polymer concentration, as for many other polyelectrolytes[2,6] and proteins. In general, it has been accepted that this constancy is due to the delicate balancing of two counteracting effects, that is, the hydrophobic effect lowering the apparent specific volume and the electrostrictional effect (or charge effect) elevating the apparent specific volume with increasing concentration.[11] If this is the case, it is interesting that the apparent specific volume is independent of concentration also for polysaccharide or its derivatives which have been considered as the hydrophilic polymer rather than the hydrophobic one. The partial specific volume, $\bar{v}^0$, was determined as the extrapolated value of apparent specific volume to zero concentration by the least-squares method and the results were listed in Table II. It is found that the values of $\bar{v}^0$ decrease with increasing degree of substitution for each derivative. The $\bar{v}^0$ value of dextran is almost consistent with the values reported in the literature.[12]

Now we can estimate the amount of hydration quantitatively from the data of the partial molal volume. Conway *et al.* and Ise and Okubo proposed the separation of the volume change by hydration of polyelectrolytes into the hydrophobic hydration effect and the electrostrictional hydration effect.[1-3] In the case of dextran derivatives the molecules have many polar groups (OH groups) attracting the water molecules by hydrogen bond, then taking account of the effect in addition to the above two effects, we may write the partial molal volume of ionic dextran derivatives, $\bar{V}^0$, in terms of the partial molal volume of polyions, V_p, and that of counterions, V_g, as follows

$$\bar{V}^0 = V_p + V_g \tag{5}$$

$$V_p = V_{\mathrm{int,p}} + H_p + P_p + E_p \tag{6}$$

$$V_g = V_{\mathrm{int,g}} + E_g \tag{7}$$

where E_p and E_g are the contributions from the electrostrictional hydration by the polyion and the counterion, respectively, H_p the contribution from the hydrophobic hydration by the polyion, P_p the contribution from the hydration around the polar groups of glucose unit, $V_{\mathrm{int,p}}$ the intrinsic polyion volume including the void, and $V_{\mathrm{int,g}}$ the intrinsic counterion volume.

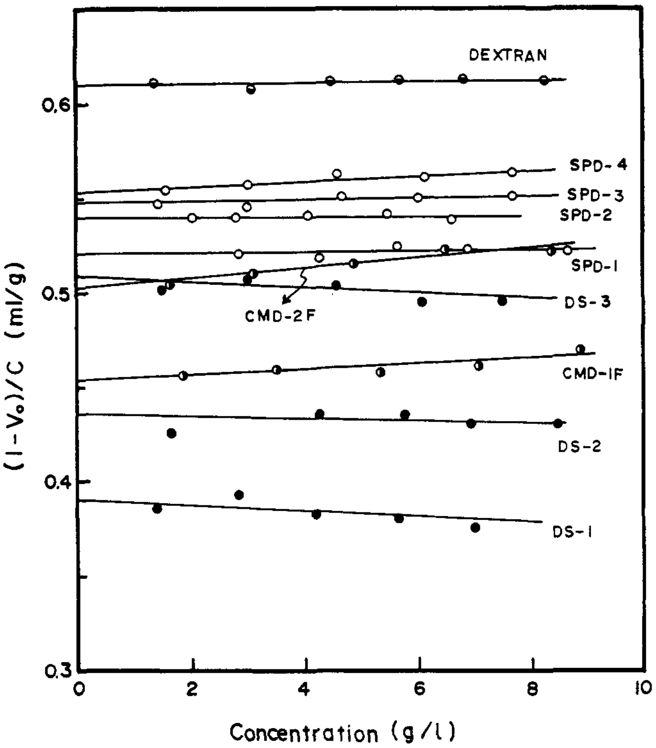

Figure 1. The relation between apparent specific volume and polymer concentration for dextran derivatives at 25°: (⊖) dextran, (○) SPD, (◑) CMD, and (●) DS.

It is one of our main purposes to clarify how the total amount of hydration of the polyions, ΔV_t ($= H_p + P_p + E_p$), is affected by the degree of substitution and the kind of substituted group on the glucose ring. It is necessary to know the values of $V_{\mathrm{int,p}}$, $V_{\mathrm{int,g}}$, and E_g in eq 6 and 7 in order to estimate ΔV_t.

The V_g term was estimated by using the following equations[13]

$$V_{\mathrm{int,g}} = 2.51 r^3 (1 + K)^3 \times \mathrm{ds} \tag{8}$$

$$E_g = -B/r(1 + K) \times \mathrm{ds} \tag{9}$$

where r is Pauling crystal radius of the counterion (in Å), 0.95 Å for Na^+, K a volume factor (=0.213), B a constant (=9.7), and ds a degree of substitution. Conway proposed a formula to estimate the intrinsic molal volume for the linear chain polyion using a cylindrical model,[1] but it is impossible to apply this formula to dextran derivatives as their molecular structure is too complicated to estimate the distance between ionizable groups on the polymer chain as compared to the vinyl-type polyelectrolytes. Therefore we estimated $V_{\mathrm{int,p}}$ by a different way, that is, the intrinsic molal volume of the solute including the void was determined by considering it to be identical with the molal volume obtained by dividing its molecular weight by the density of the crystal. We obtained 103.8 ml/monomol as $V_{\mathrm{int,p}}$ of dextran molecule by dividing the molecular weight of the repeating glucose unit by the density of D-glucose, 1.56. This value of $V_{\mathrm{int,p}}$ is very close to 101.9 ml/monomol calculated by the method of Cohn and Edsall[14] from summation of the volume of elements, *e.g.*, C = 9.9, H = 3.1, and O = 2.3 ml.

The intrinsic molal volume of dextran derivatives was obtained as the sum of the intrinsic molal volumes of dextran and substituted group. The intrinsic molal volume of carboxymethyl group was taken as 47.1 ml/$\mathrm{CH_2COO^-}$ from the density of crystalline sodium acetate, 1.518, tak-

Table II
Density and Sound Velocity Measurements for Sodium Salts of Dextran Derivatives at 25°

Dextran Deriv	Deg of Substitution	Mol Wt Monomol	$\bar{v}^0$ (ml/g)	$-\lim_{c\to 0} \frac{(\beta/\beta_0 - V_0)}{c}$	du/dc (cm l./g sec)	$-\bar{\beta}^0 \times 10^{12}$ (cm²/dyn)
Dextran	0	162.0	0.610	0.10	23.4	7.3
SPD-4	0.51	235.5	0.553	0.366	34.93	29.63
SPD-3	0.91	294.6	0.548	0.403	37.01	32.90
SPD-2	1.41	365.2	0.540	0.424	37.24	35.15
SPD-1	2.20	479.0	0.521	0.476	38.16	40.90
DS-3	0.61	224.3	0.510	0.353	24.73	30.99
DS-2	1.46	311.0	0.436	0.445	22.18	45.73
DS-1	2.54	421.2	0.390	0.492	20.56	56.46
CMD-2F	0.72	219.6	0.502	0.542	37.84	48.35
CMD-1F	1.60	290.0	0.454	0.683	44.01	67.40

Table III
Individual Molal Volumes and the Partial Molal Compressions of Dextran Derivatives at 25°[a]

Dextran Deriv	Deg of Substitution	$\bar{V}^0$	V_g	V_p	$V_{int,p}$	ΔV_t	$-\bar{V}^0\bar{\beta}^0 \times 10^9$ (ml cm²/dyn monomol)
Dextran	0	98.8	0	98.8	103.8	−5.0	0.721
SPD-4	0.51	130.2	−2.34	132.5	159.8	−27.3	3.854
SPD-3	0.92	161.4	−4.21	165.6	204.8	−39.2	5.310
SPD-2	1.41	197.2	−6.46	203.7	258.6	−54.9	6.932
SPD-1	2.20	249.6	−10.1	259.7	345.4	−85.7	10.21
DS-3	0.61	114.4	−2.79	117.2	140.6	−23.4	3.545
DS-2	1.46	135.6	−6.69	142.3	191.8	−49.5	6.201
DS-1	2.54	164.3	−11.6	175.9	257.0	−81.1	9.276
CMD-2F	0.72	110.2	−3.30	113.5	135.5	−22.0	5.328
CMD-1F	1.60	131.7	−7.33	139.0	174.2	−35.2	8.876

[a] Individual molal volumes are expressed in ml/monomol.

ing the volume of hydrogen as 3.1 ml, and that of sodium as 3.84 ml. The intrinsic molal volume of sulfate group was taken as 63.4 ml/SO_3^- from the density of $NaHSO_3$ crystal, 1.48. For SPD, we obtained the intrinsic molal volume of 112.9 ml/$CH_2CH_2CH_2SO_3^-$ by adding the volume of SO_3^- to the volume of $CH_2CH_2CH_2$, 49.5 ml (= 3 × 16.5), which was induced from the molal volume of aliphatic alcohols. The value of 16.5 ml/CH_2 used in this paper is also close to Cohn's value, 16.1 ml.[14]

According to the above procedures, we calculated $V_{int,p}$ of each derivative using the following equations

$$\text{for CMD} \quad V_{int,p} = 103.8 + 44.0 \times \text{ds} \tag{10}$$

$$\text{for DS} \quad V_{int,p} = 103.8 + 60.3 \times \text{ds} \tag{11}$$

$$\text{for SPD} \quad V_{int,p} = 103.8 + 109.8 \times \text{ds} \tag{12}$$

As shown in eq 6, the total amount of hydration, ΔV_t, depends on the value of intrinsic molal volume of polyions, $V_{int,p}$. At present, we have no satisfactory procedure to evaluate the real value of $V_{int,p}$, but we consider that our estimation method of $V_{int,p}$ based on the density of crystal would give a value close to the real $V_{int,p}$. The results obtained are listed in Table III and the values of ΔV_t are plotted against the degree of substitution in Figure 2.

First, we note that ΔV_t is negative for all derivatives. Hitherto the electrostrictional contribution, E_p, has been shown to be negative and the electrostriction per mole of water in the primary hydration shell was reported to be 2.7 ml by Conway *et al.*[1] and 2.0 ml by Yasunaga and Sasaki.[15] On the other hand, the hydration around the polar groups, P_p, is estimated to produce a volume decrease of about 1 ml/mol of water, based on the fact that in the case of dimerization of urea in water due to hydrogen-bond formation there is a volume increase of 2 ml.[16] Further, it has been reported that H_p takes also a negative value, though it depends on the kind of hydrophobic group, *e.g.*, −20 ml/mol of propane and −6 ml/mol of benzene.[17] Taking into consideration these negative values of each contribution to hydration, the more negative value of ΔV_t represents the larger amount of hydration. As mentioned above, the hydration behavior of our ionic polysaccharides is complicated because of the existence of three types of hydration around the molecule and then in this case it is difficult to perform such a separation of the total water of hydration into each contribution as may be done in the case of synthetic polyelectrolytes. But we can deduce some valuable information on the characteristic hydration of the ionic polysaccharides from the total amount of hydration.

As expected, the substitution of ionic groups for OH groups results in an increase of hydration because the effect of an ionic group on the hydration is larger than that of the OH group as explained previously. As is shown in Figure 2, the hydration increases almost linearly with increasing degree of substitution for all derivatives, as it does for carboxymethylcellulose.[6] We can obtain the following relations between the total volume change by hydration and the degree of substitution (see Figure 2)

$$\text{for CMD} \quad \Delta V_t = -5 - 21.2 \times \text{ds} \tag{13}$$

$$\text{for DS} \quad \Delta V_t = -5 - 30.3 \times \text{ds} \tag{14}$$

$$\text{for SPD} \quad \Delta V_t = -5 - 37.8 \times \text{ds} \tag{15}$$

It is worth noticing that, at the same degree of substitution, the amount of hydration increased in the order CMD < DS < SPD. The values of −21.2 and −30.3 ml in eq 13 and 14 are attributed mainly to the volume changes due to electrostriction per mole of COO^- and SO_3^- groups, respectively. The difference in the amount of hydration between CMD and DS may arise from the different electrostriction around both ionic groups. Strictly speaking, a hydrophilic ionic group such as COO^- may retain the potentiality of hydration by hydrogen bond besides electrostricted hydration, but it is difficult to distinguish such hydrogen-bonded effects from electrostrictive effects for

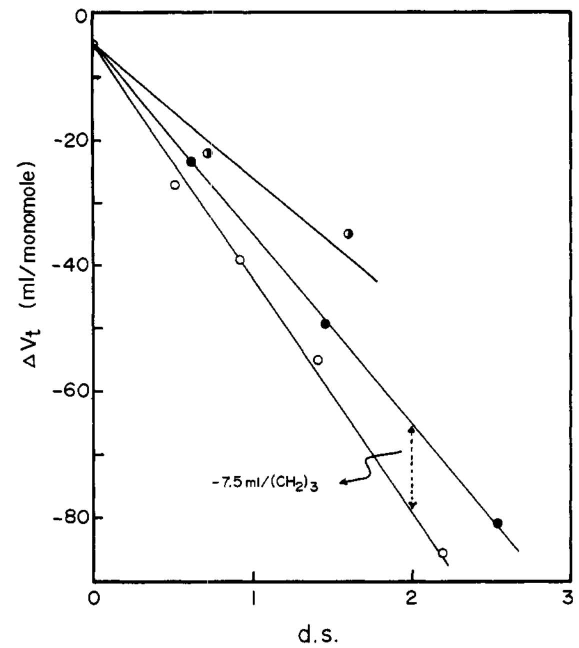

Figure 2. The relation between total volume change by hydration and degree of substitution for dextran derivatives at 25°: (◒) dextran, (◑) CMD, (●) DS, and (○) SPD.

ionic groups. So, at present, we are obliged to include such hydrogen-bond effects into electrostriction of ionic groups, as is done by many investigators.

On the other hand, the difference of ΔV_t, about −7.5 ml, between DS and SPD is ascribed to the effect of the additional hydrophobic propyl group of SPD as E_p and P_p of SPD are considered to be equivalent to those of DS. This value for the hydrophobic hydration is considerably smaller than the volume change by dissolution of propane gas into water, −20 ml/mol. This result may suggest that ionic groups adjacent to the hydrophobic groups have some inhibiting effects for the formation of icebergs.

Partial Specific Compressibility. Plots of sound velocity against the polymer concentration showed a linear relationship for aqueous solutions of dextran derivatives as well as other polyelectrolytes.[18] The concentration dependence of the sound velocity, du/dc, was calculated by the least-squares method and is listed in Table II.

The partial specific compressibility of a solute, $\bar{\beta}^0$, was calculated from the sound velocity and the density data by the method described in the Experimental Section. There were linear relationships between the values of $(\beta/\beta_0 - V_0)/c$ and c for all materials. The values of

$$\lim_{c \to 0} (\beta/\beta_0 - V_0)/c$$

obtained by an extrapolation procedure were listed in Table II. The values of $\bar{\beta}^0$ obtained are negative and decrease with increasing degree of substitution as shown in Table II and Figure 3. At the same degree of substitution, $\bar{\beta}^0$ decreases in the order SPD > DS > CMD. In the case of ionic dextran derivatives, it is difficult to determine the amount of hydration from the compressibility data because there exist three kinds of hydration, as distinguished from the case of simple ions. Therefore we introduced the following procedure to analyze the compressibility data in terms of the hydration behavior.

If e milliliters of free water is bound electrostrictionally to the ionic groups on a repeating unit of polymer chain and reduces to e' milliliters, the volume change due to the electrostriction, E_p, is expressed as $E_p = e' - e$. In the same way, $H_p = h' - h$ and $P_p = p' - p$, here h and p represent the volumes of free water which are changed to h' and p' milliliters by the hydrophobic hydration and the hydrogen-bonded hydration, respectively. Thus, substitution of these relations into eq 6 yields

$$V_p = V_{int,p} + (h' - h) + (p' - p) + (e' - e) \quad (6')$$

On the other hand, $\bar{\beta}^0$ is written as follows, where the partial molal volume is used instead of the partial specific volume

$$\bar{\beta}^0 = -(1/\bar{v}^0)(\partial\bar{v}^0/\partial P) = -(1/\bar{V}^0)(\partial\bar{V}^0/\partial P)$$

Since the partial molal volume of counterions, V_g, and the intrinsic volume of polymer, $V_{int,p}$, are considered to be almost incompressible volumes, the following equation is derived using eq 5 and 6′

$$-\bar{V}^0\bar{\beta}^0 = \partial\bar{V}^0/\partial P = \partial V_p/\partial P$$
$$= \beta_w(h + p + e) - (h'\beta_h + p'\beta_p + e'\beta_e) \quad (16)$$

where β_h, β_p, β_e, and β_w represent the adiabatic compressibilities of the water of hydrophobic hydration, hydrogen-bonded hydration, electrostricted hydration, and the free water, respectively. The amount $-\bar{V}^0\bar{\beta}^0$ corresponds to the partial molal compression, *i.e.*, the differential coefficient of the partial molal volume with pressure at infinite dilution. The $-\bar{V}^0\bar{\beta}^0$ values of all dextran derivatives are positive and increase with a degree of substitution as shown in Table III and Figure 4. The positive value of $-\bar{V}^0\bar{\beta}^0$ means an increase of the partial molal volume of the polymer with pressure and therefore corresponds to the volume change by hydration decreased with pressure per monomole of the polymer. The increase of $-\bar{V}^0\bar{\beta}^0$ with degree of substitution is not contradictory to the dependence of the partial molal volume on the degree of substitution since a larger amount of hydration is expected to produce more volume change with pressure. Figure 4 also shows that the $-\bar{V}^0\bar{\beta}^0$ value decreases in the order CMD > SPD > DS at the same degree of substitution. This result suggests that it will be necessary to take into consideration the difference of the hydration structure for each ionic group besides the total amount of hydration in order to explain reasonably the larger pressure dependence of hydration of CMD compared with SPD and

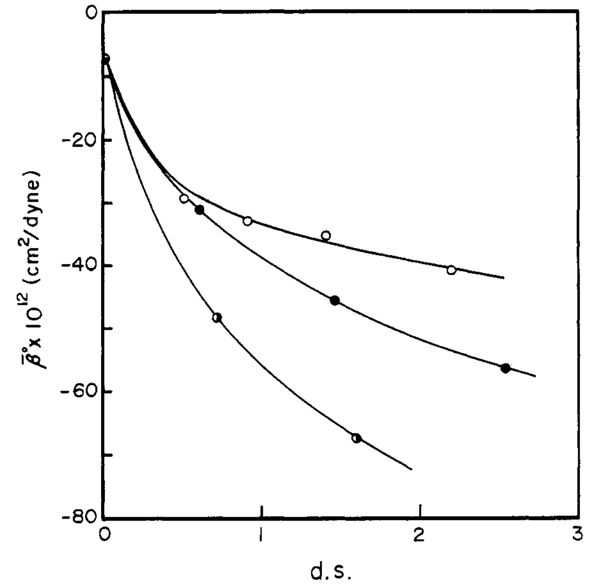

Figure 3. The relation between partial specific compressibility and degree of substitution for dextran derivatives at 25°: (◒) dextran, (◑) CMD, (●) DS, and (○) SPD.

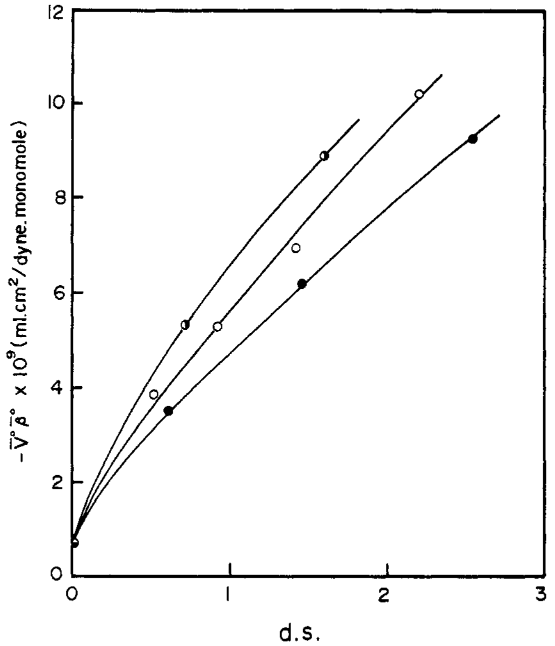

Figure 4. The relation between partial molal compression and degree of substitution for dextran derivatives at 25°: (⊖) dextran, (◑) CMD, (○) SPD, and (●) DS.

DS. The difference of $-\overline{V}^0\overline{\beta}^0$ between SPD and DS which increases with a degree of substitution may be interpreted to be caused by the additional water of hydrophobic hydration of SPD as expected.

Let us write eq 16 for DS and SPD as follows

$$-\overline{V}_{DS}{}^0\overline{\beta}_{DS}{}^0 = \beta_w(h_{DS} + p_{DS} + e_{DS}) - (h_{DS}'\beta_h + p_{DS}'\beta_p + e_{DS}'\beta_e) \quad (17)$$

$$-\overline{V}_{SPD}{}^0\overline{\beta}_{SPD}{}^0 = \beta_w(h_{SPD} + p_{SPD} + e_{SPD}) - (h_{SPD}'\beta_h + p_{SPD}'\beta_p + e_{SPD}'\beta_e) \quad (18)$$

The left-hand sides of eq 17 and 18 can be determined experimentally. Assuming that the amounts of E_p and P_p of SPD are equal to those of DS, that is, $e_{DS} = e_{SPD}$, $e_{DS}' = e_{SPD}'$, $p_{DS} = p_{SPD}$, and $p_{DS}' = p_{SPD}'$, we subtract eq 17 from 18 and obtain

$$-\overline{V}_{SPD}{}^0\overline{\beta}_{SPD}{}^0 + \overline{V}_{DS}{}^0\overline{\beta}_{DS}{}^0 = \beta_w(h_{SPD} - h_{DS}) - \beta_h(h_{SPD}' - h_{DS}') = 0.85 \times 10^{-9} \text{ (ml cm}^2\text{/dyn monomol) (see Figure 4)} \quad (19)$$

On the other hand, from the results of the volume change as mentioned in the section of the partial molal volume (see Figure 2)

$$(h_{SPD}' - h_{SPD}) - (h_{DS}' - h_{DS}) = -7.5 \text{ ml} \quad (20)$$

From eq 19 and 20 with $\beta_w = 45 \times 10^{-12}$ cm^2/dyn

$$(h_{SPD}' - h_{DS}')(\beta_h - \beta_w) = -0.51 \times 10^{-9} < 0 \quad (21)$$

Since the amount of iceberg water around SPD is larger than that of DS, that is, $(h_{SPD}' - h_{DS}') > 0$, we obtain the relation $\beta_w > \beta_h$. Therefore the water of hydrophobic hydration or icebergs becomes less compressible than the free water, which is consistent with Conway's proposition.[19]

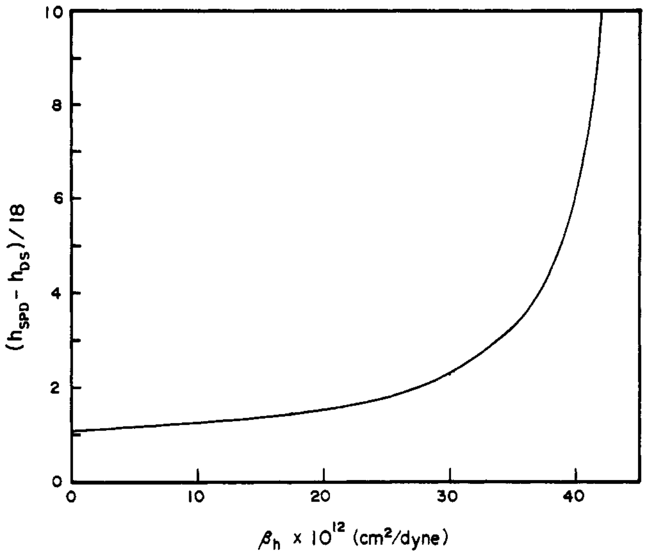

Figure 5. Hydrophobic hydration number around propyl group of SPD as a function of adiabatic compressibility of icebergs at 25°.

Though the value of β_h cannot be determined from this experiment, we can estimate the difference of hydrophobic hydration between SPD and DS as a function of β_h using eq 20 and 21 as shown in Figure 5. The values of $(h_{SPD} - h_{DS})/18$ may be considered to correspond to the number of water of hydrophobic hydration around $CH_2CH_2CH_2$ groups of SPD. We would obtain the values of 1.3-1.5 as the hydration number per mole of propyl group on taking the adiabatic compressibility of ice, $\beta_{ice} = 12\text{-}18 \times 10^{-12}$ cm^2/dyn as β_h. But this hydration number (corresponding to the volume change of about −5.5 ml/mol of water) is too small to account for the volume change of −7.5 ml/mol of propyl group considering the volume change by electrostrictional hydration is −2.7 ml/mol of water at the most. This gives an important suggestion that the water of hydrophobic hydration should be more compressible than ice.

It has been known that β_p is close to β_{ice}[8,20] and that the electrostricted water has a very small compressibility.[21] Then we may suppose $\beta_e < \beta_p < \beta_h < \beta_w$ as the order of the adiabatic compressibility of the water participating in the hydration. Determination of the β_h value, if possible in the future, would help to clarify the structure of water around the hydrophobic groups.

Acknowledgment. The authors thank Dr. A. Shinoda, Director of Research Institute of Meito Sangyo Co., Ltd., Nagoya, for supplying the materials investigated.

References and Notes

(1) B. E. Conway, J. E. Desnoyers, and A. C. Smith, *Phil. Trans. Roy. Soc. London, Ser. A*, **256**, 389 (1964).
(2) N. Ise and T. Okubo, *J. Amer. Chem. Soc.*, **90**, 4527 (1968).
(3) J. Lawrence and B. E. Conway, *J. Phys. Chem.*, **75**, 2353 (1971).
(4) J. Lawrence and B. E. Conway, *J. Phys. Chem.*, **75**, 2362 (1971).
(5) N. Ise, *Advan. Polym. Sci.*, **7**, 536 (1971).
(6) C. Tondre and R. Zana, *J. Phys. Chem.*, **76**, 3451 (1972).
(7) H. Noguchi, K. Gekko, and S. Makino, *Macromolecules*, **6**, 438 (1973).
(8) K. Gekko and H. Noguchi, *Biopolymers*, **10**, 1513 (1971).
(9) Y. Suzuki and H. Uedaira, *Bull. Chem. Soc. Jap.*, **43**, 1892 (1970).
(10) M. G. Greenspan and C. E. Tschiegg, *Rev. Sci. Instrum.*, **28**, 897 (1956).
(11) W. Y. Wen and S. Saito, *J. Phys. Chem.*, **68**, 2639 (1964).
(12) J. Brandrup and E. H. Immergut, "Polymer Handbook," Interscience Publishers, New York, N. Y., 1966, p IV-111.
(13) P. Mukerjee, *J. Phys. Chem.*, **65**, 740 (1961).
(14) E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides," Academic Press, New York, N. Y., 1943, p 155.
(15) T. Yasunaga and T. Sasaki, *Nippon Kagaku Zasshi*, **72**, 87 (1951).
(16) W. Kauzmann, *Advan. Protein Chem.*, **14**, 1 (1959).

(17) W. L. Masterson, *J. Chem. Phys.*, **22**, 1830 (1954).
(18) P. Roy-Chowdhury, *J. Appl. Polym. Sci.*, **12**, 751 (1968); *J. Polym. Sci., Part A2*, **7**, 1451 (1969).
(19) B. E. Conway and R. E. Verrall, *J. Phys. Chem.*, **70**, 3952 (1966).
(20) H. Shiio, *J. Amer. Chem. Soc.*, **80**, 70 (1958).
(21) A. Passynsky, *Acta Physiocochim. USSR*, **8**, 385 (1938).

Specific Solvent Effects in Swollen Polymer Networks

C. U. Yu and J. E. Mark*

Department of Chemistry and the Macromolecular Research Center, The University of Michigan, Ann Arbor, Michigan 48104. *Received August 20, 1973*

ABSTRACT: Stress-strain isotherms at 25° have been determined for uniaxially elongated poly(dimethylsiloxane) networks in the unswollen state and swollen consecutively with each of the following very dissimilar diluents: low molecular weight dimethylsiloxane fluid, *n*-hexadecane, 2,4-dichlorotoluene, and *n*-octyl acetate. Five constant composition experiments were carried out, at values of the volume fraction v_2 of polymer of 1.00, 0.80, 0.60, 0.50, and 0.35. At $v_2 = 0.80$, the stress-strain isotherms were found to be independent of the nature of the diluent; at lower values of v_2, however, these isotherms were significantly different, thus demonstrating the existence of a "specific solvent effect" in swollen polymer networks. Interpretation of these data in terms of the statistical theory of rubber-like elasticity gave results in good agreement with previously reported specific solvent effects on the unperturbed dimensions of uncross-linked poly(dimethylsiloxane) chains in solution. In neither case, however, do these effects correlate well with the cohesive energy density or dielectric constant of the diluent or solvent medium.

In the study of the relationship between stress and strain in elongated polymer networks, measurements on samples containing diluent are usually more highly regarded than those carried out on unswollen specimens.[1-3] The primary reason for this preference is the observation[1-5] that stress-strain isotherms on swollen networks much more closely approach the form predicted by the theory of rubberlike elasticity.[1-3,6-8] An additional, and possibly related advantage is the relative rapidity with which swollen networks appear to reach elastic equilibrium.[9-13] Such diluents in swollen polymer networks have been treated customarily as entirely inert media in that their presence has been accounted for by simple geometric modification of the elastic equation of state to account for the reduction in the number of chains passing through unit cross-sectional area and the deformation of these chains to the new, increased volume of the swollen network.[1,2] According to the most general form[6-8] of the statistical or kinetic-molecular theory of rubberlike elasticity, however, the stress exhibited by a deformed polymer network depends on the unperturbed dimensions $\langle r^2 \rangle_0$ of its constituent chains. As is now well known, $\langle r^2 \rangle_0$ for a particular polymer of specified chain length generally depends on temperature because of differences in energy between various conformational states accessible to the chain backbone.[5,14,15] In addition, however, these dimensions are now known to depend at least in some cases on the *environment* of the chains.[16-24] Briefly, the unperturbed dimensions are obtained most reliably by viscometric or light-scattering measurements on the polymer chains at the Θ point, at which the chain co-volume is effectively zero and perturbations due to excluded volume are absent.[1] Although in such studies $\langle r^2 \rangle_0$ is found to be at least approximately independent of the nature of the solvent medium in the case on nonpolar polymers, sizable differences are frequently observed in the case of significantly polar chains.[16-26] These differences, known loosely as "specific solvent effects," are thought to originate in solvent-induced changes in conformational energy, and thus in configuration and size, of the polymer chains. Such changes could arise from the dependence of intramolecular electrostatic interactions on the dielectric constant of the medium,[27-29] or from a less well understood direct interaction between solvent molecules and polymer chain segments.[22,30-32]

In any case, the demonstration[16-26] of a specific solvent effect on $\langle r^2 \rangle_0$ from measurements on polymer solutions, and the presence of $\langle r^2 \rangle_0$ in the theoretical elastic equation of state indicates that specific solvent (diluent) effects should also occur in appropriately chosen swollen polymer networks, with a discernible effect on stress-strain relationships at constant temperature. Unfortunately, there are relatively little data in the literature for testing this prediction; the only relevant studies pertain to networks prepared from natural rubber[10,11] and from polyethylene,[30] swollen, as required for comparison, with each of a number of diluents. In these cases, significant specific solvent effects were not observed but these results are not at all conclusive with regard to the possible existence of such an effect since the polymers employed are essentially nonpolar and there is probably considerable uncertainty in some of the results obtained using diluents of rather high volatility.

The purpose of the present study was therefore to determine stress-strain relationships at constant temperature for polymer network–diluent systems in which there would be maximum likelihood of observing specific solvent effects, if present. Networks prepared from poly(dimethylsiloxane) (PDMS) $(CH_3)_3Si[OSi(CH_3)_2]_xOSi(CH_3)_3$ were chosen as the best candidates for the following reasons. (i) PDMS chains are significantly polar,[28,29] and the unusual values obtained for the equation-of-state parameters of the polymer[33] and the thermodynamic properties of its solutions[34] suggest that polymer–diluent interactions might be particularly prominent in swollen PDMS networks; (ii) the wide-ranging solubility of the uncross-linked polymer[35] indicates that a variety of chemically dissimilar solvents would be suitable as network diluents; (iii) the polymer is easily cross-linked into networks which are readily extensible at room temperature and have excellent stability over extended periods of time,[36] and finally, (iv) the approximate magnitude of the specific solvent effect to be expected in swollen PDMS networks can be estimated from a summary[19] of reported values of $\langle r^2 \rangle_0$ for PDMS chains in a variety of Θ solvents, in particular from values obtained from light-scattering intensities of PDMS chains