BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1038—1044 (1972)

Effects of Chain Molecules on the Temperature of the Maximum Density of Water

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(Received November 4, 1971)

The shifts in the temperature of the maximum density of water produced by the addition of small amounts of oligomers of polyethylene glycol and polyethylenimine and other related compounds were determined by dilatometry. These effects were interpreted in terms of the change in the structure of water around the various solute molecules in connection with their chain length. It was found that, as the chain length increases, the extent of the modification of the water structure by the chain molecules decreases because of the hydrophobic contact between ethylene groups. The apparent specific expansibility of the solute in the neighbourhood of 4°C was also evaluated as a function of the concentration.

The nature and role of water structure in aqueous polymer solutions have been subjects of great interest and controversy for a long time.[1] For example, recently Klotz[2] has discussed in detail the hydrophobic interactions between water and the alkyl groups of polymers; then, from the results of their near-infrared spectra measurements in H_2O/D_2O mixture, Worley and Klotz concluded that polyvinylpyrrolidone fits into the group of hydrogen-bonded structure makers.[3] On the contrary, Goldfarb and Rodriguez[4] have suggested, from their thermodynamic data, that the hydrated sheath around polyvinylpyrrolidone in water is not "ice-like," but is to be classified as part of the classical scheme of solute hydration.

An alternative approach to the problem of polymer-water interaction may be to examine the effect of chain length on certain properties of aqueous solutions of oligomers. From this point of view, the solubilities of hydrocarbons in oligomeric polyethylenimine solutions have been determined by Okubo and Ise.[5] Their solubility data indicate that the hydrophobicity of the oligomers increases with an increase in the molecular weight. More recently, the volumetric properties of aqueous solutions of the oligomers of polyethylene glycol and polypropylene glycol have been investigated by Sandell and Goring.[6] The apparent specific expansibility, which they have regarded as a measure of the structural effect of a solute,[7] increases with an increase in the chain length; that is, the extent of the hydrophobic hydration is reduced as the chain length increases. This has been interpreted in terms of the increasing hydrophobic contact between ethylene groups.

Since the hydrogen-bonded structure of water is greatly sensitive to the temperature, it seemed that it would be useful to examine the temperature dependence of some thermodynamic properties in order to specify the structural phenomena of aqueous polymer solutions.

In the present paper, we will report some results concerning the effects of the addition of chain molecules on the temperature of the maximum density (TMD) of water. The phenomenon of the TMD of water at 3.98°C has been regarded as coming from the balance of the increase in volume resulting from the thermal expansion and the decrease in volume resulting from the breakdown of the hydrogen-bonded low-density water structure.[1,8,9] Although, in general, the presence of various kinds of solutes depresses the TMD from 3.98°C, it is also well known that some alcohols elevate the TMD in very dilute

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[1] J. L. Kavanau, "Water and Solute-Water Interactions," Holden-Day, Inc., San Francisco (1964).

[2] I. M. Klotz, *Federat. Proc.*, **24**, *Suppl.* 15, s-24 (1965).

[3] J. D. Worley and I. M. Klotz, *J. Chem. Phys.*, **45**, 2868 (1966).

[4] J. Goldfarb and S. Rodriguez, *Makromol. Chem.*, **116**, 96 (1968).

[5] T. Okubo and N. Ise *J. Phys. Chem.*, **73**, 1488 (1969).

[6] L. S. Sandell and D. A. I. Goring, *J. Polym. Sci.*, *Part A*-2 **9**, 115 (1971).

[7] J. L. Neal and D. A. I. Goring, *J. Phys. Chem.*, **74**, 658 (1970).

[8] D. Eisenberg and W. Kauzmann, "The Structure and Properties of Water," Oxford Univ. Press, London (1969).

[9] "Hydrogen-Bonded Solvent Systems," ed by A. K. Covington and P. Jones, Taylor, and Francis Ltd., London (1968).

solutions.[10–13] This observation implies that these alcohol molecules stabilize the hydrogen-bonded intermolecular structure of water. Wada and Umeda[13] and Franks and Watson[14] have shown that the depression in the TMD produced by the addition of small amounts of many organic compounds is less than that to be expected when ideal mixing takes place, and that, as a rule, this effect is more pronounced when the number of carbon atoms within the solute molecules increases. Thus, the solutes which show a tendency to raise the TMD may be assumed to stabilize the structure of water.

The purpose of this work is to make an attempt to clarify the interactions between polymers and water on the basis of the measurements of the TMD and in connection with the concept of the structural change of water.

Experimental

Procedure. Bicapillary-type dilatometers with a capacity of about 80 m*l* and with capillary tubes 0.7 mm in diameter were used to measure the temperature dependence of the volumes of the aqueous solutions. Measurements were made with a cathetometer at approximately 0.3∼0.5°C intervals in the range ±2°C from the TMD. The temperature of the thermostat bath was maintained with a precision of ±0.002°C, and the temperatures corresponding to the measured volumes were read on a Beckmann thermometer. In order to correct the thermal expansion of the dilatometer itself, the shift in the TMD, $\Delta\theta$, produced by the addition of a solute was determined graphically, according to the method of Wada and Umeda,[13] by comparing the meniscus height-temperature curve of the solution with that of pure water. By using this method, the maximum error in estimating $\Delta\theta$ was ±0.02°C. It has been found that the values of $\Delta\theta$ obtained preliminarily with regard to the solutions of both sodium chloride and ethylene glycol are in good agreement with the literature values.[13,15]

The densities of the pure solutes were determined at 5, 15, 25, 35, and 45°C using Ostwald-type pycnometers with a volume of about 20 m*l*.

Materials. The polyethylene glycol (PEG) was furnished by the Sanyo Kasei Co. The PEG-200 and PEG-400 (the average molecular weights are 200 and 400 respectively) were dried under reduced pressure and were used without further purification. The PEG-20000 was recrystallized from methyl ethyl ketone and was dried at room temperature under a vacuum. The polyethylenimine (PEI) was purified by passing its dilute solution through columns containing cation and anion exchange resins in the hydrogen and hydroxide forms respectively. Its molecular weight was estimated viscometrically to be about 2000. The ethylene glycol (EG) was a chromatographically pure reagent, and the ethylenediamine (ED) and triethylamine (TEA) were guaranteed reagents. These materials were dried over molecular sieve and were used without further purification. The diethylene glycol (DEG), triethylene glycol (TEG), ethylene glycol dimethyl ether (EGDME), diethylene glycol dimethyl ether (DEGDME), triethylene glycol dimethyl ether (TEGDME), diethylenetriamine (DT), triethylenetetramine (TT), and tetraethylenepentamine (TP) were fractionally distilled. The water used to prepare the solutions was distilled and then purified by passing it through a column of cation-anion exchange resin mixtures.

Results and Discussion

The specific volumes of the pure solutes at various temperatures are given in Table 1. From these data, the specific expansibilities, $\partial v_2/\partial T$, at 4°C can be

TABLE 1. SPECIFIC VOLUME, v_2, AND SPECIFIC EXPANSIBILITY, $\partial v_2/\partial T$, AT 4°C OF PURE SOLUTES

Solute	v_2 (m*l* g^{-1})					$\partial v_2/\partial T \times 10^3$ (m*l* g^{-1} deg^{-1})
	5°	15°	25°	35°	45°	
EG	0.88967	0.89520	0.90087	0.90660	0.91248	0.547
DEG	0.88713	0.89280	0.89846	0.90433	0.91025	0.557
TEG	0.88071	0.88685	0.89300	0.89926	0.90563	0.606
PEG-200	0.87959	0.88596	0.89230	0.89868	0.90522	0.628
PEG-400[a]	—	—	—	—	—	0.646
PEG-20000	—	—	—	—	—	(0.66)
EGDME[a]	—	—	—	—	—	1.346
DEGDME[a]	—	—	—	—	—	1.064
TEGDME[a]	—	—	—	—	—	0.947
ED	—	1.10796	1.11966	1.13163	1.14388	1.126
DT	1.03803	1.04750	1.05694	1.06647	—	0.943
TT	1.00782	1.01624	1.02445	1.03281	—	0.832
TP	0.99473	1.00273	1.01036	1.01818	—	0.780
PEI	—	—	—	—	—	(0.62)
TEA	1.34836	1.36528	1.38263	1.40080	—	1.647

a) The values of $\partial v_2/\partial T$ of these solutes were calculated from the unpublished density data by T. Nakajima.

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10) J. P. McHutchison, *J. Chem. Soc.*, **1926**, 1898.

11) N. Gregg-Wilson and R. Wright, *J. Phys. Chem.*, **35**, 624 (1931).

12) A. G. Mitchell and E. F. K. Wynne-Jones, *Discuss. Faraday Soc.*, **15**, 161 (1953).

13) G. Wada and S. Umeda, This Bulletin **35**, 646, 1797 (1962).

14) F. Franks and B. Watson, *Trans. Faraday Soc.*, **63**, 329 (1967).

15) "International Critical Tables," Vol. III, McGraw-Hill, New York (1933), p. 107.

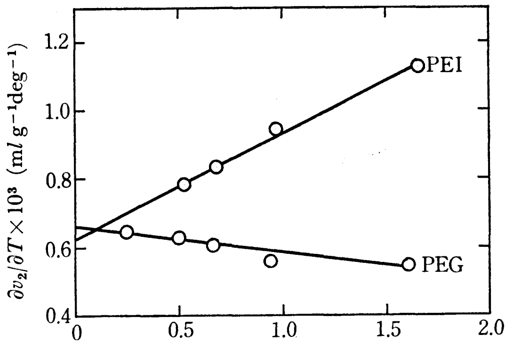

Fig. 1. Plots of specific expansibility at 4°C *vs.* the reciprocal of molecular weight of the oligomers.

evaluated by the least-square method; the values are given in the last column of Table 1. The specific volumes of high polymers in the liquid state are not known, so the $\partial v_2/\partial T$ values of PEG-20000 and PEI were estimated roughly by extrapolating the corresponding values of the respective oligomers to an infinite molecular weight, as is illustrated in Fig. 1.

The shifts, $\Delta\theta$, in the TMD produced by the addition of various solutes are summarized in Table 2. The concentration is expressed in terms of the weight fraction in order to facilitate the comparison of the behavior of polymers with that of low-molecular-weight analogues.

The quantitative analysis of $\Delta\theta$ in terms of the water-structural concept has been proposed by Wada and

Table 2. The shifts in TMD and the apparent specific expansibilities in the neighbourhood of 4°C at various weight fractions

Solute	$w \times 10^2$	$\Delta\theta$ (deg)	$\Delta\theta_{\text{str}}$ (deg)	$\partial\phi_2/\partial T \times 10^3$ (ml g^{-1} deg^{-1})
EG	0.4232	−0.22	−0.07	0.81±0.07
	0.5727	−0.30	−0·10	0.81±0.05
	0.7575	−0.41	−0.14	0.84±0.04
	1.0544	−0.55	−0.18	0.81±0.03
	1.5899	−0.83	−0.26	0.80±0.02
	2.1588	−1.17	−0.40	0.83±0.02
DEG	0.4504	−0.20	−0.04	0.69±0.07
	0.5977	−0.27	−0.06	0.70±0.05
	0.9017	−0.42	−0.10	0.72±0.03
	1.0327	−0.48	−0.11	0.72±0.03
	1.4325	−0.70	−0.18	0.75±0.02
	2.3016	−1.12	−0.28	0.74±0.02
TEG	0.2840	−0.12	−0.01	0.66±0.11
	0.5040	−0.24	−0.04	0.74±0.06
	0.6469	−0.32	−0.07	0.77±0.04
	0.9076	−0.46	−0.10	0.78±0.03
	1.2236	−0.65	−0.17	0.82±0.03
	2.2177	−1.22	−0.34	0.84±0.02
PEG-200	0.1787	−0.11	−0.04	0.96±0.17
	0.3264	−0.20	−0.07	0.95±0.10
	0.5948	−0.33	−0.09	0.86±0.05
	0.8130	−0.45	−0.12	0.86±0.04
PEG-400	0.1319	−0.08	−0.03	0.94±0.23
	0.3379	−0.20	−0.06	0.92±0.09
	0.5463	−0.34	−0.11	0.97±0.06
	0.8555	−0.54	−0.18	0.98±0.03
PEG-20000	0.3357	−0.22	−0.07	1.02±0.09
	0.5752	−0.38	−0.14	1.02±0.06
	1.2382	−0.83	−0.30	1.03±0.03
EGDME	0.1347	−0.04	0.08	0.46±0.23
	0.2726	−0.08	0.16	0.46±0.11
	0.4292	−0.18	0.19	0.65±0.07
	0.4958	−0.20	0.23	0.63±0.06
	0.6276	−0.25	0.29	0.62±0.05
	0.7770	−0.32	0.36	0.64±0.04
	1.0282	−0.42	0.48	0.63±0.03
	1.5267	−0.70	0.64	0.70±0.02
DEGDME	0.5848	−0.33	0.07	0.88±0.06
	0.8516	−0.48	0.11	0.87±0.04
	1.1625	−0.65	0.15	0.86±0.03
	1.6526	−0.95	0.20	0.88±0.02
	2.0689	−1.21	0.23	0.89±0.02
TEGDME	0.5559	−0.30	0.04	0.84±0.06
	0.8191	−0.46	0.04	0.87±0.04
	1.3529	−0.77	0.06	0.88±0.03
ED	0.1263	−0.07	0.02	0.86±0.24
	0.3426	−0.19	0.06	0.86±0.09
	0.5477	−0.33	0.07	0.93±0.06
	0.8811	−0.53	0.11	0.93±0.04
	1.2344	−0.78	0.12	0.97±0.03
DT	0.0983	−0.05	0.01	0.79±0.31
	0.1772	−0.08	0.03	0.70±0.18
	0.5299	−0.25	0.07	0.73±0.06
	1.0397	−0.50	0.13	0.74±0.03
	1.5302	−0.74	0.20	0.74±0.02
	2.4478	−1.25	0.27	0.78±0.02
TT	0.7412	−0.33	0.07	0.69±0.05
	1.0523	−0.47	0.10	0.69±0.03
	1.5883	−0.72	0.14	0.70±0.02
	1.9005	−0.87	0.16	0.70±0.02
	2.7827	−1.32	0.21	0.72±0.01
TP	0.2167	−0.10	0.01	0.72±0.14
	0.4075	−0.18	0.02	0.69±0.09
	0.7812	−0.33	0.06	0.06±0.04
	2.0290	−0.88	0.16	0.66±0.02
	2.5220	−1.13	0.16	0.68±0.01
	3.4949	−1.63	0.18	0.70±0.01
PEI	0.1247	−0.07	−0.02	0.88±0.24
	0.2258	−0.12	−0.03	0.83±0.14
	0.3988	−0.24	−0.08	0.94±0.08
	0.5354	−0.28	−0.07	0.81±0.06
	0.8395	−0.46	−0.12	0.85±0.04
TEA	0.0932	0.02	0.12	−0.33±0.33
	0.1944	0.00	0.21	0.00±0.16
	0.5141	−0.07	0.48	0.21±0.06
	1.2898	−0.39	0.99	0.47±0.03
	1.8690	−0.73	1.28	0.60±0.02

Umeda[13] and has been extended by Franks and Watson.[14] The specific volume, v, of a solution is expressed by:

$$v = (1-w)v_1 + wv_2 + \Delta v_w^{\mathrm{M}} \tag{1}$$

where v_1 and v_2 are the specific volumes of water and a pure solute respectively, and where Δv_w^{M} is the excess volume of mixing referred to a mixture of the solute weight fraction, w. The temperature dependence of v_1 in the vicinity of the TMD can be given by a parabolic function:[13]

$$v_1 = v_1{}^*[1+\alpha_1(T-3.98)^2] \tag{2}$$

where $v_1{}^*$ is the specific volume of water at 3.98°C and where α_1 is the coefficient relating to the thermal expansion. By inserting Eq. (2) into Eq. (1), and differentiating with respect to temperature, and then from the condition: $\partial v/\partial T=0$ at the TMD, one obtains the following relation:

$$\Delta\theta = (T-3.98) = -\frac{w\partial v_2/\partial T}{2(1-w)v_1{}^*\alpha_1} - \frac{\partial\Delta v_w^{\mathrm{M}}/\partial T}{2(1-w)v_1{}^*\alpha_1} \tag{3}$$

The first term, denoted by $\Delta\theta_{\mathrm{id}}$, on the right-hand side of Eq. (3) indicates that, for ideal solutions, $\Delta\theta$ is always negative and is proportional to the concentration as long as for very dilute solutions. The second term, denoted by $\Delta\theta_{\mathrm{str}}$, is referred to the temperature dependence of the excess volume and may be attributed to the change in water structure caused by adding various solutes.

The values of $\Delta\theta_{\mathrm{str}}$ have been evaluated for various solutes.[13,14] In general, it appears that the values of $\Delta\theta_{\mathrm{str}}$ are large and positive for such solutes as monofunctional alcohols and amines, whereas more hydrophilic solutes such as ethylene glycol and dioxane produce negative $\Delta\theta_{\mathrm{str}}$ values. In other words, the sign and magnitude of $\Delta\theta_{\mathrm{str}}$ depend mainly on the hydrophilic-hydrophobic balance within the respective solute molecules, or are due to some kinds of water-structure modifications.

There have been various discussions with respect to the structure of water in a pure liquid state and in aqueous solutions. At present, however, no satisfactorily reasonable interpretation and models have been proposed.[1,8,9,16,17] In the present analysis, the so-called two-state model was adopted as a basis for discussion; it is assumed that water is an equilibrium mixture of bulky hydrogen-bonded species and dense unbonded species, and also that the introduction of a small quantity of non-polar molecules or groups into aqueous solutions shifts the equilibrium between the two species from dense species to bulky species.

The effect of a solute on TMD may be interpreted in terms of the difference in the specific expansibility of the pure solute and the apparent specific expansibility of the solute in water. The specific volume of a solution is also expressed using the apparent specific volume, ϕ_2, of a solute as follows:

$$v = (1-w)v_1 + w\phi_2 \tag{4}$$

Then, we obtain the following equation instead of Eq. (3):

$$\Delta\theta = -\frac{w}{2(1-w)v_1{}^*\alpha_1}\frac{\partial\phi_2}{\partial T} \tag{5}$$

Combining Eqs. (3) and (5) yields;

$$\frac{\partial\Delta v_w^{\mathrm{M}}}{\partial T} = w\left(\frac{\partial\phi_2}{\partial T} - \frac{\partial v_2}{\partial T}\right) \tag{6}$$

Since the hydrogen-bonded structure of water is broken down rapidly with a rise in the temperature, and since, accordingly, the amounts of unbonded water mole-

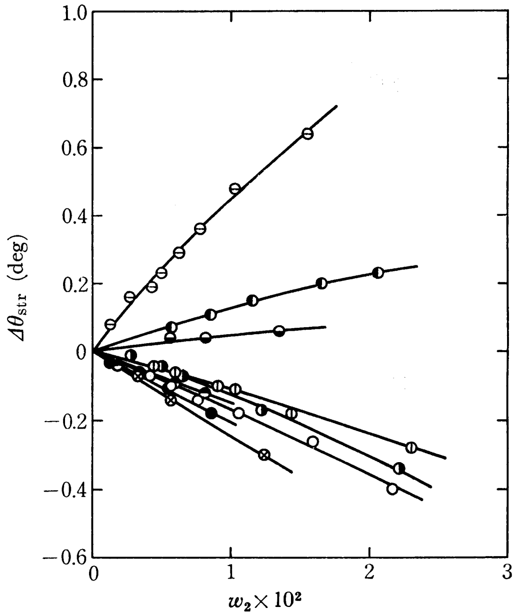

Fig. 2. Variation of $\Delta\theta_{\mathrm{str}}$ with the concentration. ○, EG; ⦶, DEG; ◑, TEG; ◓, PEG-200; ●, PEG-400; ⊗, PEG-20000; ⊖, EGDME; ◐, DEGDME; ◒, TEGDME.

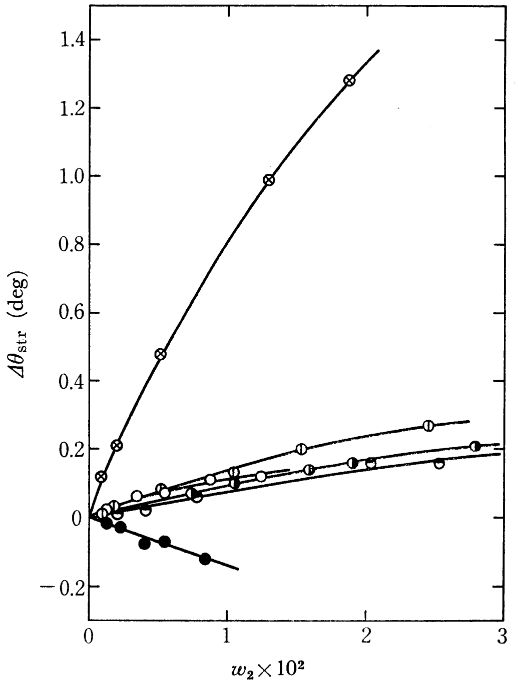

Fig. 3. Variation of $\Delta\theta_{\mathrm{str}}$ with the concentration. ○, ED; ⦶, DT; ◑, TT; ◓, TP; ●, PEI; ⊗, TEA.

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16) H. S. Frank, *Federat. Proc.*, **24**, *Suppl.* 15, s-1 (1965).

17) H. S. Frank, *Science*, **169**, 635 (1970).

cules with a higher density are increased, the increase in the apparent specific volume of a hydrophobic solute in aqueous solution caused by the increase in temperature might to some extent be canceled out in comparison with a case where no special hydrophobic interaction, the so-called "hydrophobic hydration," takes place. Therefore, when the solute is a structure-stabilizing one, the value of $\partial\phi_2/\partial T$ is smaller than that of $\partial v_2/\partial T$; namely, a positive $\Delta\theta_{\text{str}}$ value can be derived from Eq. (6).

In Table 2 and in Figs. 2 and 3, the values of $\Delta\theta_{\text{str}}$ obtained are shown as a function of the weight fraction.[18] From the results shown in Fig. 2, it is clear that, for a series of PEG oligomers, the $\Delta\theta_{\text{str}}$ values are all negative over the entire concentration range studied and that they change according to their chain lengths in the following order:

DEG>TEG>PEG-200>EG>PEG-400>PEG-20000

Unfortunately, little is yet known about the influence of such a polar substance on the structure of water, but the fact that negative $\Delta\theta_{\text{str}}$ values are obtained may indicate that these solutes disrupt the intermolecular structure of water because of the formation of strong hydrogen bonds between solutes and water. It seems that the increase in temperature produces such larger ϕ_2 values as a result of the disruption of the solute-water hydrogen-bonding, which itself results in the volume contraction around the hydroxyl groups. If this is true, the $\Delta\theta_{\text{str}}$ value should become negative according to Eq. (6).

As regards the hydrophilic-hydrophobic balance within a solute molecule, molecules of longer chain length should become more hydrophobic than lower-molecular-weight analogues in this series, because of the relative decrease in the contribution from the hydrophilic terminal hydroxyl groups. The above sequence observed for PEG oligomers is, however, just the opposite of what might be expected from this idea, except for the case of EG. As will be discussed in detail later, we propose another scheme of interpretation, *i.e.*, a concept of hydrophobic contact between ethylene groups.

Figure 3 shows the $\Delta\theta_{\text{str}}$ values for the PEI oligomers and TEA. The latter is expected to behave as a typical hydrophobic solute in water. In fact, TEA produces a strikingly large positive $\Delta\theta_{\text{str}}$, which is comparable in magnitude to those produced by monohydric alcohols[13] or dialkylamines.[14] It is observed with PEI oligomers that the $\Delta\theta_{\text{str}}$ changes according to their chain lengths in the following order:

DT>ED>TT>TP>PEI

which is quite similar to the sequence for the PEG oligomers. However, in contrast to the PEG oligomers, the values of $\Delta\theta_{\text{str}}$ are slightly positive except for the case of PEI. This difference suggests that the hydrogen bond between water and the hydroxyl group of the PEG oligomers is stronger than that between water and the amino group of the PEI oligomers. This may be accounted for on the basis that the more electronegative oxygen atom is generally able to form a stronger hydrogen bond than is the less electronegative nitrogen atom.

It could, however, be emphasized that too much significance should not be found in the difference in $\Delta\theta_{\text{str}}$ because of the choice of the standard state.[19,20] In the present analysis, the pure liquid state of the solute was used as the standard state in order to calculate $\partial v_2/\partial T$ and $\Delta\theta_{\text{str}}$. For the purpose of a more accurate discussion of the solute-water interaction, one should use the hypothetical value of $\partial v_2/\partial T$ in an infinitely dilute aqueous solution (in other words, under the condition that no solute-solute interaction takes place) instead of in the pure liquid state. Especially when liquids exhibits significant intermolecular interactions, the adoption of the pure liquid state as the standard has its disadvantages. We should not ignore this situation in comparing the behavior of the oligomers of the PEG with that of the PEI, since the former possesses a much greater ability of solute-solute hydrogen-bonding than the latter; this is suggested by their high viscosities and the characteristic variation in their specific expansibilities with the increase in the chain length for the PEG oligomers, as is shown in Fig. 1. This may also be closely related to the fact that the $\Delta\theta_{\text{str}}$ values of various alcohols and amines do not always increase in a regular manner with the number of carbon atoms within the solute molecules. It may, at any rate, be permissible to consider that the difference in $\Delta\theta_{\text{str}}$ indicates at least a relative difference in the solute-water interaction so far as the chain-length dependence of $\Delta\theta_{\text{str}}$ for the oligomers of the homologous series is concerned, as we have done in this study.

As is shown in Fig. 2, for the series of glycol dimethyl ethers the $\Delta\theta_{\text{str}}$ values are all positive, decreasing more rapidly in magnitude with the increase in chain length than for the series of the PEG and PEI oligomers. The positive $\Delta\theta_{\text{str}}$ value suggests a comparatively stronger hydrophobic hydration caused by the terminal methyl groups. This is confirmed by the results of the limiting partial molar volumes of various glycols in aqueous solutions by Nakanishi *et al.*,[21] who stated that such glycol molecules as 1,2-ethanediol and 1,3-propanediol mix "substitutionally" with water, whereas, when one of the hydroxyl groups is not located at the end of the molecule (*e.g.*, 1,2-propanediol or 1,3-butanediol), the "interstitial" contribution due to a possible cavity occupation by a methyl group increases.

As has been described above, ED and EG give rise

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[18] In order to calculate $\Delta\theta_{\text{str}}$ as a first approximation, the value of $\partial v_2/\partial T$ at 4°C is always employed in the present analysis, since it can be considered that there is no effect of the variation of $\partial v_2/\partial T$ in a small range of temperature (the maximum value of $\Delta\theta$ obtained in this experiment is -1.63°C). Also, the use of $\partial v_2/\partial T$ which are estimated roughly by a extrapolation method for the high polymers is believed not to result in a large error in calculating $\Delta\theta_{\text{str}}$, or at least this has no influence upon the present discussion relating to the chain length dependence.

[19] F. Franks and H. T. Smith, *Trans. Faraday Soc.*, **64**, 2962 (1968).

[20] General Discussion in Ref. 9, p. 222.

[21] K. Nakanishi, N. Kato, and M. Maruyama, *J. Phys. Chem.*, **71**, 814 (1967).

to unordinary values of $\Delta\theta_{str}$, and EGDME produces a particularly large positive $\Delta\theta_{str}$ value. This observation suggests that, in the case of these small molecules with only one ethylene group, the nature of the terminal group may be one of the decisive factors in the interactions between the solute and the water molecules.

Thus, the results on the $\Delta\theta_{str}$ values of these oligomer solutions prove that the hydrophobic interaction of a chain molecule with water decreases as the chain length increases, provided that the interaction is not affected remarkably by the terminal group. It is plausible to consider that the effect of the chain length on the hydrophobicity is due to the conformational change of a chain molecule. Recently, Neal and Goring[7] measured the temperature dependence of the apparent specific volume, *i.e.*, the apparent specific expansibility, $\partial\phi_2/\partial T$, for various aqueous solutions; they proposed that this quantity might be a useful measure of the effect of a nonelectrolyte on the structure of water. Subsequently, they could show the increase in $\partial\phi_2/\partial T$ with an increase in the chain length for both oligomers of polyethylene glycol and polypropylene glycol.[6] That is to say, the hydrophobic character of a chain molecule decreases with an increase in the chain length. More recently, the partial molar volumes of the series of glycol dimethyl ethers in aqueous solutions have been measured at various temperatures by Nakajima *et al.*[22] According to their analysis, the partial molar volume of the ($-CH_2CH_2O-$) group can be calculated from the differences in the partial molar volumes between DEGDME and EGDME and also between TEGDME and DEGDME. The value obtained from TEGDME is greater than those obtained from DEGDME and EGDME. This fact suggests that the extent of the hydrophobic hydration of these chain molecules in aqueous solutions decreases with an increase in the chain length, if one accepts the hypothesis that such a hydration occurs with an overall economy of space. These results agree very well with the results of our TMD measurements. The most reasonable interpretation of this effect may be that, with an increase in the chain length, the hydrophobic contact between ($-CH_2CH_2-$) groups takes place more easily and that, consequently, the relative decrease in hydrophobic interaction is observed because of the reduction of the ($-CH_2CH_2-$) area which is accessible to water, as was proposed by Sandell and Goring.[6]

By using Eq. (5), the values of $\partial\phi_2/\partial T$ in the neighbourhood of 4°C at various concentrations can be calculated from the TMD data, which are summarized in the last column of Table 2. The maximum error in $\partial\phi_2/\partial T$ was estimated on the basis of the accuracy in determining TMD: ± 0.02°C. Some results are shown in Figs. 4 and 5, in which the values for several alcohols calculated from the TMD data by Wada and Umeda[13] are also included. Of course, the values of $\partial\phi_2/\partial T$ at various concentrations cannot be evaluated at a constant temperature by this method; moreover, the accuracy of $\partial\phi_2/\partial T$ is not satisfactory because of the very low concentrations. The data shown in Figs. 4 and 5, however, may be good enough for us to discuss some qualitative tendency of these values in connection with the hydrophobic character of the solutes. The fact that the $\partial\phi_2/\partial T$ values of all the PEG oligomers increase with an increase in the chain length, except for EG, accords qualitatively with the results which were directly measured by Sandell and Goring. For the PEI oligomers, on the other hand, this is not the case. The variation in $\partial v_2/\partial T$ with the chain length is exceedingly larger for the PEI

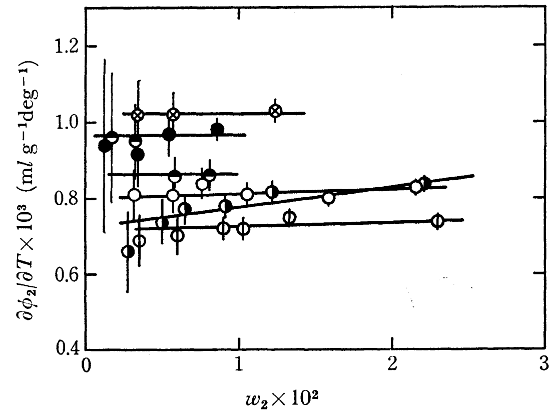

Fig. 4. Concentration dependence of $\partial\phi_2/\partial T$ for PEG oligomers; ○, EG; ⦶, DEG; ◑, TEG; ◓, PEG-200; ●, PEG-400; ⊗, PEG-20000.

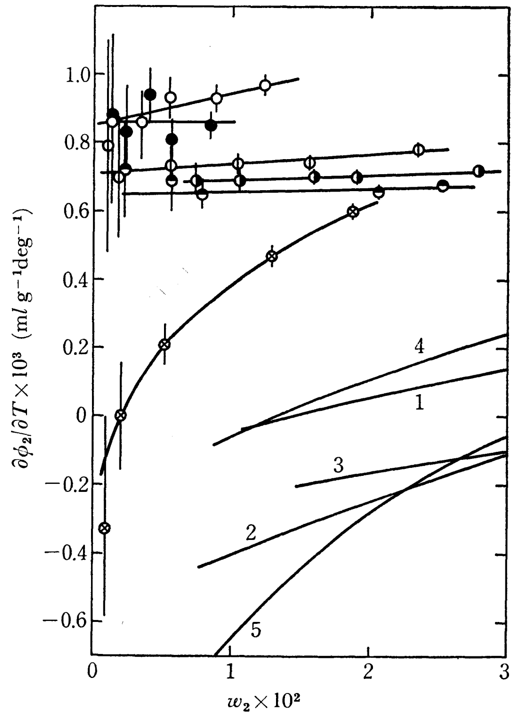

Fig. 5. Concentration dependence of $\partial\phi_2/\partial T$ for PEI oligomers, TEA and some alcohols (the data for alcohols are all calculated from Wada and Umeda, Ref. 13); ○, ED; ⦶, DT; ◑, TT; ◓, TP; ●, TEI; ⊗, TEA; 1, MeOH; 2, EtOH; 3, *iso*-PrOH; 4, *sec*-BuOH; 5, *tert*-BuOH.

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[22] T. Nakajima, T. Komatsu, and T. Nakagawa, *Repts. Progr. Polym. Phys. Japan*, **14**, 1 (1971).

oligomers than for the PEG oligomers, as is shown in Fig. 1; therefore, the variation in the $\partial\phi_2/\partial T$ values with the chain length seems to be largely due to the difference in $\partial v_2/\partial T$ values, though there exists a problem in the choice of the standard state, as has been mentioned above. In such a case it may be inadequate to use the quantity $\partial\phi_2/\partial T$ as a measure of the effect of a solute molecule on the structure of water.[23]

Figures 4 and 5 show the characteristic tendencies of $\partial\phi_2/\partial T$ for various solutes. The solutes which produce small positive or negative $\Delta\theta_{\text{str}}$ values, such as the chain molecules used in this experiment, give rise to a slight concentration dependence of $\partial\phi_2/\partial T$, whereas those which produce large positive $\Delta\theta_{\text{str}}$ values, such as TEA and many monohydric alcohols, bring about a striking concentration dependence of $\partial\phi_2/\partial T$. The latter have been regarded as hydrogen-bonded-structure makers and will give rise to a larger hydrophobic hydration than the former.

It is well known that the apparent specific volume of a hydrophobic substance in an aqueous solution decreases with its concentration so long as the concentration is low. This behavior has been interpreted in terms of "mutual salting-in"[25] or "mutual co-operative stabilization."[26] According to Franks and Smith,[26] the non-polar solutes form complete or partial clathrate cage systems, resulting in a contraction in the net volume. When two solute molecules approach each other at a suitable distance, such cage systems are stabilized co-operatively and, consequently, ϕ_2 decreases with a rise in the concentration. Therefore, the slope of the ϕ_2-concentration curve becomes more negative as the temperature is lowered or as the sizes of the non-polar groups of the solute molecules become larger. This phenomenon is the same as with the larger concentration dependence of $\partial\phi_2/\partial T$ of the strongly hydrophobic solutes. Thus, the concentration dependence of $\partial\phi_2/\partial T$ may also be regarded as a useful measure of the structural effect of a solute molecule from the viewpoint of solute-solute interaction.

One could find from Eq. (5) that a positive $\Delta\theta$ is equivalent to the negative expansibility. As has been mentioned in the introduction, this anomalous behavior should be considered as an evidence for the stabilization of the water structure surrounding the non-polar groups of a solute molecule. In fact, the negative expansibility has been observed directly with *tert*-butyl alcohol and *sec*-butyl alcohol in very dilute aqueous solutions.[19] As is shown in Fig. 5, it is evident that this phenomenon should also be observed in the very dilute aqueous solutions of many monohydric alcohols and possibly TEA.

Finally, it should be pointed out that our conclusion concerning chain molecule-water interaction is quite similar to that of Sandell and Goring,[6] but it may conflict with the explanation by Okubo and Ise of their solubility results.[5] The solubilities of naphthalene and biphenyl in aqueous solutions of PEI and its oligomers (ED, DT, TT, TP) increase with increases in their chain length. From these results they have concluded that the so-called "iceberg" formation of water molecules may be facilitated by an increasing degree of polymerization. It is difficult to solve the problem of these conflicting results. It can, however, be proposed that the solubility behavior of a non-polar co-solute in aqueous solutions of the chain molecules may be of a rather complicated nature as a result, for instance, of the conformational change of the solute molecules themselves. A more systematic investigation regarding the solubility behavior of nonelectrolytes in aqueous polymer solutions, and especially its temperature dependence, remains a subject for future study.

The authors wish to thank Mr. Toshio Nakajima for his helpful discussion. The present work has been supported in part by a Grant for Scientific Research from the Ministry of Education.

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[23] According to the data of Sandell and Goring,[6] the values of $\partial v_2/\partial T$ for PEG oligomers are independent of the chain lengths; in such a case $\Delta\theta_{\text{str}}$ must be in parallel with $\partial\phi_2/\partial T$. Our own data obtained by pycnometry, however, indicate that $\partial v_2/\partial T$ are clearly dependent on the chain lengths, as shown in Fig. 1. That is to say, it is not always advantageous to discuss any solute-water interaction in terms of $\partial\phi_2/\partial T$ or $\Delta\theta$ (not $\Delta\theta_{\text{str}}$). For example, it should be misleading to conclude from the measurements of $\Delta\theta$ alone that the quaternary alkylammonium halides, which are regarded as typical structure stabilizing solutes at room temperature, disrupt the hydrogen-bonded structure of water at low temperatures.[24]

[24] A. J. Darnell and J. Greyson, *J. Phys. Chem.*, **72**, 3021 (1968); see also, T. S. Sarma and J. C. Ahluwalia, *ibid.*, **74**, 3547 (1970).

[25] J. E. Desnoyers and M. Arel, *Can. J. Chem.*, **45**, 359 (1967).

[26] F. Franks and H. T. Smith, *Trans. Faraday Soc.*, **63**, 2586 (1967).