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SHORT COMMUNICATION

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# Volume and compressibility changes for short poly(ethylene glycol)–water system at various temperatures

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**Abstract** The volume and compressibility changes on mixing of water and poly(ethylene glycol 400) were measured with a vibration densimeter and a sing-around velocimeter over the whole mole fraction at various temperatures. The apparent molar expansibility and compressibility of water were calculated and characterized by distinct maxima and minima, respectively. These results may be attributed to the hydration behavior of the polymer chain.

**Key words** PEG – water – volume – expansibility – compressibility

## Introduction

Poly(ethylene glycol) (PEG) is a nonionic linear polymer and consists of hydrophilic oxygen and hydrophobic ethylene units. Its high solubility in water makes it a very interesting material. The structure of aqueous solutions of PEG is an important subject from the viewpoint of polymer chemistry and surface and colloid sciences, since the hydration structure of this chain is closely related to the size and shape of the micelles and the phase behaviour in surfactant and nonionic polymer solutions [1, 2].

There has been much interest in the PEG–water system [3–7]. Blandamer et al. pointed out that the distance between alternate oxygen atoms in the PEG chain is similar to the next-nearest-neighbor distance between oxygen atoms in water [3]. Then this idea has been developed by Kjellander and Flourin who suggested that the ethylene group is encaged by a dynamic network of water molecules and, at the same time, hydrogen bonds are formed between water and the ether oxygen [4]. Karlström [8] has proposed a model that suggests that the segments of the PEG chain form two conformations due to the difference in rotation around C–C and C–O bonds. Based on this model the phase equilibrium can be interpreted in terms of the balance between these conformational forms; i.e., the trans conformations are formed at higher temperatures and the gauch conformations are favored with decreasing temperature or increasing polarity of solvents [9]. Thus, the hydration structure of the PEG chain is a fundamental factor for understanding its conformation and stability, since the hydrogen-bonded structure of water is sensitive to temperature [10].

It is well known that the structure of water is more or less influenced by the addition of nonelectrolytes. The volume or compressibility behaviour of dilute aqueous nonelectrolyte solutions has been discussed by many authors in connection with the structural change of water. A few investigations have been performed by using density and ultrasound velocity measurements to obtain information about the solution structure of the PEG–water system [11–15]. However, studies of water dissolved in PEG (i.e., the volume, expansibility and compressibility of water in the PEG solution) at various temperatures are scarce. In order to understand more precisely the contributions of the hydration on volume and compressibility changes for this system, it is desirable to study aqueous solutions in PEG-rich regions where one need not any longer take into account the tetrahedral structure of water molecules. We chose the short PEG chain (molecular weight 400) to make the measurements possible over the whole mole fraction range at various temperatures. The purpose of the present

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study is to clarify the factors contributing to the volume and compressibility properties in the short PEG–water system over the whole mole fraction range.

## Experimental

PEG (for gas chromatography) was purchased from E. Merck Science (FRG) and was used without further purification. The mean molecular weight of PEG is 400. Distilled and deionized water was used.

The solution densities, $\rho$, were measured using an oscillating-tube densimeter (Anton Paar DMA 60/602). The temperature around the density measuring cell was maintained by circulating water from a constant-temperature bath. Thermal stability of the bath was better than $\pm 1 \times 10^{-2}$ °C. The density could be determined with accuracy of $\pm 3 \times 10^{-6}$ g cm$^{-3}$.

Ultrasonic velocity measurements in solutions were made by using a homemade sing-around velocimeter operating at 5 MHz, which is capable of an accuracy of 1 cm s$^{-1}$. The cell of the velocimeter was placed deep in a water bath maintained at $\pm 0.002$ °C by a laboratory-made controller using a $Y$-cut quartz as a temperature sensor. Details of the apparatus, their calibrations, and experimental procedures used have been described previously [16, 17]. The solutions were prepared by successive addition of a weighed amount of a pure solute into the measuring cell containing a known quantity of solvent. The temperature range investigated was from 5 to 45 °C.

## Results and discussion

The excess molar volume of a mixture of liquid components 1 and 2 is calculated from the density data by Eq. (1):

$$V^E = (x_1M_1 + x_2M_2)/\rho - (x_1M_1/\rho_1) - (x_2M_2/\rho_2) , \quad (1)$$

where $x$ is the mole fraction, $M$ is the mole mass, $\rho$ is the density of the solution, and the subscripts 1 and 2 refer to liquid components 1 and 2, respectively. In this study the mole fraction and molar mass of the PEG monomer group (–$CH_2CH_2O$–) were used to evaluate the contribution of hydration per PEG monomer unit. The density of water was taken from the data given by Kell [18].

In Fig. 1 the values of $V^E$ are plotted as a function of the PEG mole fraction per monomer unit at various temperatures. The $V^E$ values are negative over the whole mole fraction and become more negative as the temperature decreases. This volumetric behavior is consistent with that reported in the literature [14].

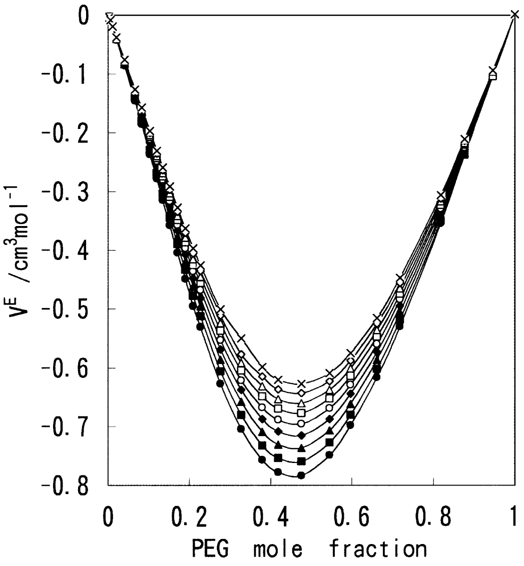

**Fig. 1** Excess molar volumes for the PEG–water system at several temperatures as a function of the PEG mole fraction: (●) 5 °C, (■) 10 °C, (▲) 15 °C, (◆) 20 °C, (○) 25 °C, (□) 30 °C, (△) 35 °C, (◇) 40 °C, (×) 45 °C

The apparent molar volume of the component 2 is given by Eq. (2).

$$V_{\phi_2} = \{(x_1M_1/x_2)(\rho_1 - \rho)/\rho_1\rho\} + M_2/\rho . \quad (2)$$

Figure 2 shows the plots of the apparent molar volumes $V_{\phi_w}$ of water in an aqueous PEG solution at various temperatures as a function of the PEG mole fraction. The values of $V_{\phi_w}$ decrease monotonically with the addition of PEG into water. Figure 3 provides the apparent molar expansibilities $E_{\phi_w}$ $(= \Delta V_{\phi_w}/\Delta T)$ of water at various temperatures over the whole mole fraction range, where the $E_{\phi_w}$ values were calculated from the difference between the $V_{\phi_w}$ values at two temperatures. The curves of $E_{\phi_w}$ are characterized by a maximum, and with the decrease in temperature, this maximum becomes more distinct and occurs at a lower PEG concentration. This result suggests that a sort of hydration complex is formed in the aqueous solution around the maximum concentration of $E_{\phi_w}$. Thus, the water molecules in the PEG-rich region may be incorporated into the PEG chains to form the structured hydration framework at a lower temperature.

The adiabatic compressibilities, $\kappa$, were calculated from the solution sound velocities $u$ and densities $\rho$ using Eq. (3).

$$\kappa = 1/(\rho u^2) . \quad (3)$$

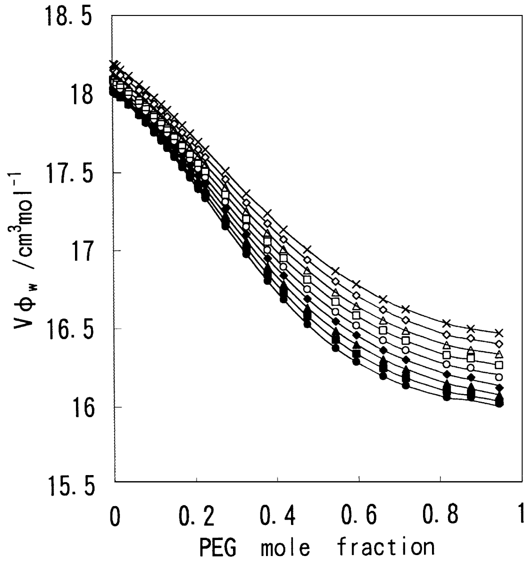

**Fig. 2** Apparent molar volumes of water at several temperatures as a function of the PEG mole fraction: (●) 5 °C, (■) 10 °C, (▲) 15 °C, (◆) 20 °C, (○) 25 °C, (□) 30 °C, (△) 35 °C, (◇) 40 °C, (×) 45 °C

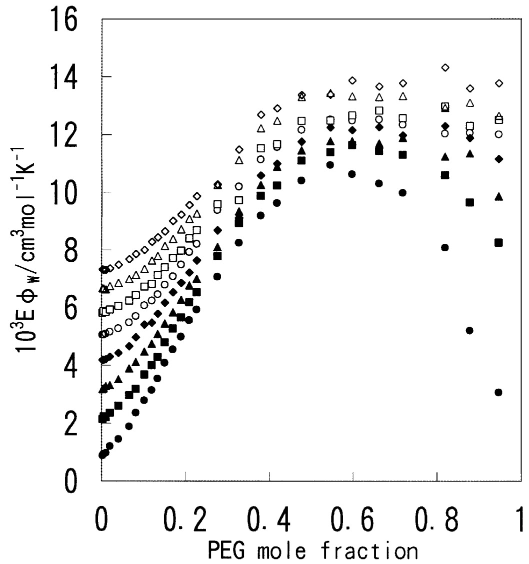

**Fig. 3** Apparent molar expansibilities of water at several temperatures as a function the PEG mole fraction: (●) 7.5 °C, (■) 12.5 °C, (▲) 17.5 °C, (◆) 22.5 °C, (○) 27.5 °C, (□) 32.5 °C, (△) 37.5 °C, (◇) 42.5 °C

The sound velocities of pure water were taken from the data reported by Del Grosso and Mader [19]. The apparent molar adiabatic compressibilities $K_{\phi_2}$ of component 2 were determined from the density and adiabatic compressibility of solution using the following equation:

$$K_{\phi_2} = \{(x_1 M_1/x_2)(\kappa\rho_1 - \kappa_1\rho)/\rho_1\rho\} + M_2\kappa/\rho \; , \qquad (4)$$

where $\kappa_1$ is the compressibility of the solvent (component 1).

Figure 4 shows the concentration variation of sound velocity for the aqueous PEG solution at various temperatures. As seen in Fig. 4 the measured values of sound velocity $u$ in the pure PEG decrease with the increase in temperature, which is completely opposite to that in water. In Fig. 5, the apparent molar adiabatic compressibilities $K_{\phi_w}$ of water at various temperatures are plotted as a function of the PEG mole fraction. The most noteworthy feature is that the values of $K_{\phi_w}$ show a shallow minimum in the PEG-rich region. This minimum becomes more distinct and shows a tendency to shift to a lower PEG concentration as the temperature is lowered.

In mixtures of water with PEG, it is necessary to consider various interactions between components, that is, attractive interactions due to the hydrogen-bond formations between ether oxygen of the PEG chain–water, water–water, and repulsive interaction between water and the methylene group of PEG (hydrophobic hydration). As a general rule, the attractive interactions bring about a reduction in both volume and compressibility and repulsive interactions are accompanied by opposite changes. It appears that this general rule is by no means clear when aqueous solutions at water-rich regions are considered, since the well-known tetrahedral structure of water (water–water hydrogen bonding) results in an increase in volume and compressibility.

In PEG-rich regions, we observed that there is a shallow minimum in $K_{\phi_w}$ values. In these regions one need not take into account the effects of the well-known tetrahedral structure of water. Therefore, we would expect that the minimum behavior of $K_{\phi_w}$ values studied here can be interpreted more simply in terms of general attractive and repulsive interactions described above. The stabilization of the hydration structure by the hydrogen-bonding between ether oxygen of PEG and water molecules is strengthened as water molecules are added into the pure PEG solvent and expected to reach the structured hydration framework. The minimum behavior of $K_{\phi_w}$ may be attributed to the balance between the attractive effect of the stabilization by the hydrogen-bonding (ether oxygen of PEG–water interaction) and the repulsive effect of the methylene group–water interaction. This repulsive effect of the methylene group–water interaction may explain the increase in $K_{\phi_w}$ values beyond the shallow minimum. The maximum and minimum behavior of $E_{\phi_w}$ and $K_{\phi_w}$, respectively, may be explained by the formation of a sort of hydration complex like inverse micelle that water molecules are incorporated into PEG chains.

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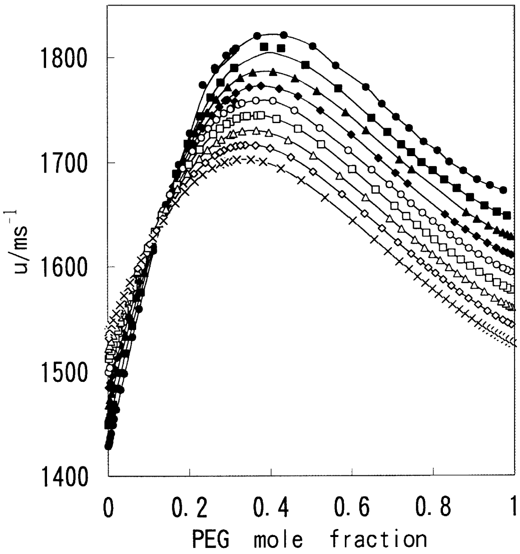

**Fig. 4** Sound velocity for the PEG–water system at several temperatures as a function the PEG mole fraction: (●) 5 °C, (■) 10 °C, (▲) 15 °C, (◆) 20 °C, (○) 25 °C, (□) 30 °C, (△) 35 °C, (◇) 40 °C, (×) 45 °C

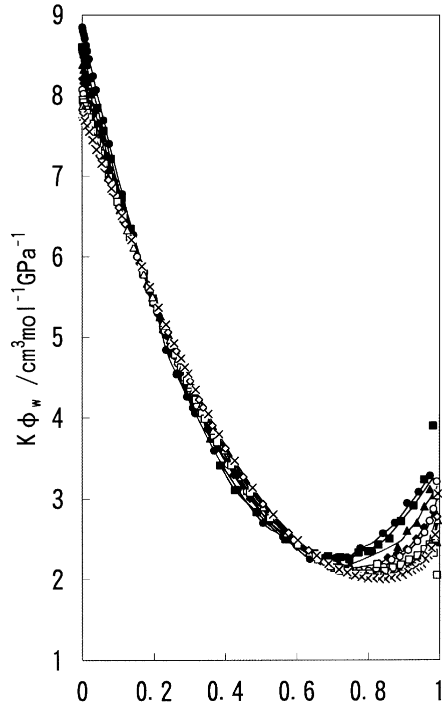

**Fig. 5** Apparent molar adiabatic compressibilities of water at several temperatures as a function of the PEG mole fraction: (●) 5 °C, (■) 10 °C, (▲) 15 °C, (◆) 20 °C, (○) 25 °C, (□) 30 °C, (△) 35 °C, (◇) 40 °C, (×) 45 °C

**Table 1** Mole fraction $X_{\mathrm{m}}^{*)}$ and ratio of molecule (group) at $X_{\mathrm{m}}$ for the PEG–water system at various temperatures

| $T$ (°C) | $X_{\mathrm{m}}$ | $H_2O/CH_2CH_2O$ |
|---|---|---|
| 5 | 0.637 | 0.57 |
| 10 | 0.747 | 0.34 |
| 15 | 0.750 | 0.33 |
| 20 | 0.750 | 0.33 |
| 25 | 0.776 | 0.29 |
| 30 | 0.785 | 0.27 |
| 35 | 0.818 | 0.22 |
| 40 | 0.826 | 0.21 |
| 45 | 0.832 | 0.20 |

PEG mole fraction at which the absolute value of $K_{\phi_{\mathrm{w}}}$ is minimum.

Table 1 shows the PEG mole fraction $X_{\mathrm{m}}$ corresponding to the minimum in $K_{\phi_{\mathrm{w}}}$ values and the ratio of the number of water molecules and the PEG monomer group in a hydration framework at $X_{\mathrm{m}}$. It should be noted that the minimum in $K_{\phi_{\mathrm{w}}}$ shows a tendency to shift to a lower PEG mole fraction and that the ratio of the water molecule and the PEG group in the structured hydration framework varies to a higher water ratio as the temperature is lowered. This result suggests that there are several types of possible hydrogen-bonding between the PEG chain and water molecules. For example, a hydrogen-bonded bridge by a water molecule between the adjacent ether oxygen atoms, or that by a water molecule between the ether oxygen atoms separated by three monomer groups [20], where the number of water molecules per monomer group corresponds to 0.5 ~ 0.33. Consequently, the compressibility behavior of water may support the temperature-dependent hydrogen-bonding and reflect the conformation changes of polymer segments for this short PEG–water system.

## Conclusions

The studies of the volume and compressibility changes of PEG compound in water have provided us with a wealth of information about the solution structure of the PEG–water system. However, the studies of water dissolved in PEG (i.e., the volume, expansibility and compressibility of water in the PEG solution) are scarce. It was found that there are the distinct maxima and minima in the apparent molar expansibility and compressibility of water for the short PEG–water system, respectively. Moreover, we observed the temperature-dependence of these maxima and minima. These behaviors may reflect the conformation change of the polymer chain.

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