EFFECT OF HYDROPHILIC SURFACES ON THE INTIMATE PROPERTY OF WATER

A.K.M. Ahsanullah* and Mohd. Eshaque Mian

Physics Division, PCSIR Laboratories, Karachi 39

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Precise measurements of thermal expansion of columns of dilute solutions of two long-chain polymers have been carried out with various concentrations, ranging from 0 to 500 ppm polyox, in the temperature range between -2°C and 10°C. It is found that there occurs a definite shift of the point of maximum density of water on the addition of a very small quantity of polyox in water. The maximum lowering of the point of maximum density of water to 1.7°C occurs at 40 ± 10 ppm of polyox, with an increase of about 1% in the absolute density of water at the point of maximum density.

It is tentatively suggested that the water molecules are able to arrange themselves in an orderly way around the polymer molecules, presumably forming a skin around the polymer chains. This ordering of water molecules, its range and depth, is dependent on the specific concentration and upon the molecular weight of polymer. An estimate of the effective depth of ordering is made, which comes out to be of the order of 300 A° to 400 A°.

It has been reported in an earlier communication[1] that the temperature of maximum density of water is lowered from 4 to 1.7°C by the addition of 50 ppm polyox in water. An increase of about 1% in the absolute density of water at the point of maximum density has also been observed. These observations tentatively suggest that (a) a very small amount of long-chain polymer is able to modify the intimate structure of water by a measurable amount, and (b) the maximum density is under the control of forces or potentials exerted over a considerable distance by the presence of a suitable solute.

In order to make a further study of these possibilities, the measurements of thermal expansion of columns of very dilute solutions of two polymers (polyoxyethylene) of molecular weight 4,000,000 and 6,000,000 have been carried out with various concentrations ranging from 0 to 500 ppm polyox, and are presented in this communication.

Experimental

The measurement of thermal expansion of columns of liquid is carried out by an especially made glass dilatometer, using a precision capillary and having provision for inserting an accurate thermometer (readable to 0.01°C) in the bulb of the dilatometer. The wide end of the dilatometer is completely sealed off by inserting the thermometer lid, while an auxiliary capillary of shorter length (10 cm in length) is suitably attached to the dilatometer to facilitate the filling of experimental liquid into the dilatometer, as shown in Fig. 1.

The filling technique as depicted in Fig. 1. consists of a small bottle "A" containing the experimental liquid, which is connected to the

*Now at: Metric Cell, Industries Division, Government of Pakistan, Room No. 44, CDA Block 2, Islamabad.

open end of the main capillary "a" while the shorter capillary "b" is connected with an air suction pump "C" through the flow bulb (or booster bulb) "B". By adjusting the rate of suction, it is possible to fill the dilatometer, free from air-bubbles as well as atmospheric impurities. At the time of filling, the bore of the main capillary "a" of the dilatometer is kept in a slanting position with the open end a little above the horizontal, and the position is just reversed while emptying (i.e. capillary "b" takes the position of "a"). As soon as the dilatometer is completely filled with the experimental liquid, the open end of the short capillary is sealed, while the open end of the main capillary is covered with a suitable cap to avoid evaporation of the test liquid, thus virtually making it a closed system.

The dilatometer is then supported inside the thermostatic bath (Townson and Mercer) by dipping it well inside the liquid, so that only two centimeters of the open end of the main capillary "a" remains above the liquid level. The temperature of the thermostatic bath is controlled to ±0.003°C, and it is therefore possible to determine the exact temperature of the test liquid within 0.01°C without difficulty. The length increment of the liquid column is measured with a reliable cathetometer, readable to 0.001 cm. The length increment of the liquid column is taken arbitrarily from 0°C, and the thermal expansion ($\Delta V \times 10^4/V_o$) is then determined by use of a readily deduced formula of the type:

$$\frac{\Delta V}{Vo} = \frac{\pi r^2 \cdot \Delta L}{(V_I - \pi r^2 Lo)} = \frac{\Delta L}{\left(\dfrac{V_I}{\pi r^2} - Lo\right)}$$

where V_I be the volume of dilatometer, L and Lo be the corresponding length of liquid column at t°C and 0°C respectively and r be the radius of the capillary. The quantity $\pi r^2 Lo$ ($\simeq V_I/1000$), is a small correction term, and accurate determina-
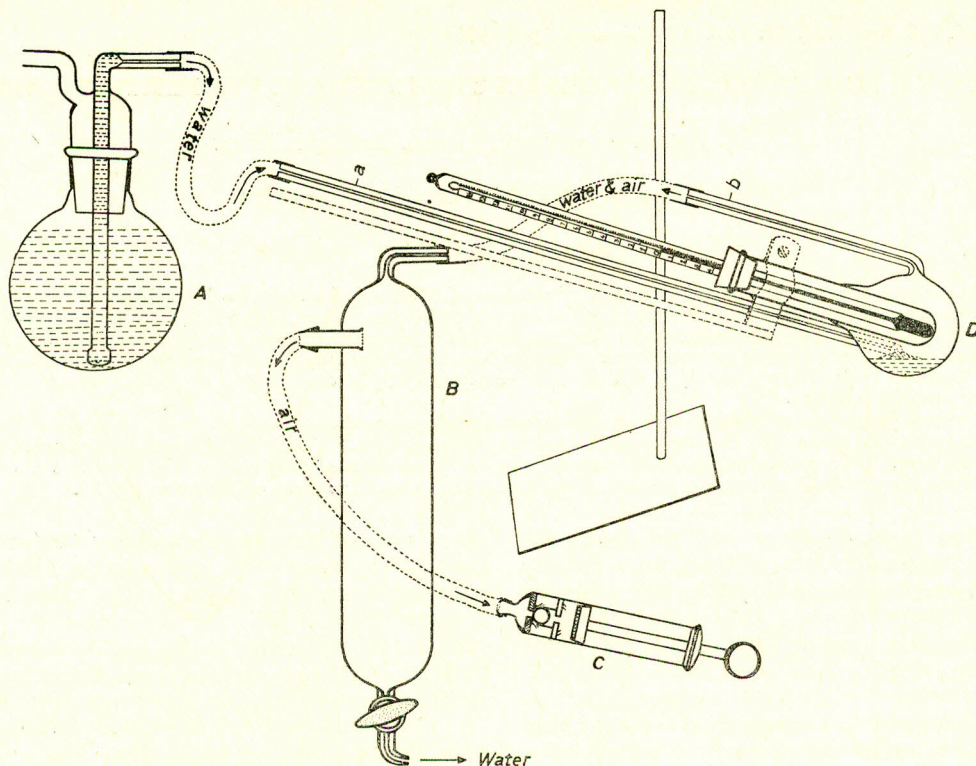
Fig. 1.—Elaborate arrangement for filling the dilatometer with experimental liquid.   A, firitted wash bottle;
B, flow bulb; C, air pump (vacuum); D, dilatometer.

tion of $\Delta V/Vo$ depends mainly on the precise determination of r, ΔL and V_I. The radius of the capillary r is determined by measuring the length of a known mass of mercury thread with a travelling microscope, and the volume V_I of the dilatometer is precisely determined by taking the weight when empty and when filled with conductivity water at a suitable temperature.

Experimental Results with Water Containing 0 *to* 500 *ppm Polyox (mol wt 4,000,000).*

Before starting the actual experiment with solutions of polymer polyoxyethylene, the dilatometer had been calibrated by taking a series of measurements of thermal expansion of columns of pure conductivity water, and the point of maximum density of water in these experiments was found to be consistently $4.00° \pm 0.02°$C.

Various water-polyox solutions are prepared by adding calculated quantity of powdered polyoxyethylene (obtained from Union Carbide Co. Ltd., England) to thrice-distilled water (by weight). For comparison with earlier data, the measurements are repeated for 50 ppm polyox in water, and data for 75 and 100 ppm in water are collected thereafter. The results are shown in Fig. 3a,

while Fig. 2 is reproduced from earlier communication.[1] All the measurements are carried out between 10 and –2°C. The temperature stability is of the order of $\pm 0.003°$C, whereas the reproducibility in the measurements of length increment is of the order of ± 0.003 cm which gives an accuracy of 5×10^{-5} in the individual determination of $\Delta V \times 10^4/Vo$. It is readily observed from the graphs of Fig. 3a that the point of maximum density of water containing 50 ppm is lowered to $1.7° \pm 0.2°$C, while it is found to occur at $3.4°$C for 75 and 100 ppm. This shows that the greatest lowering of the point of maximum density of water occurs approximately at 50 ppm. The absolute value of the maximum densities of water containing 50, 75 and 100 ppm polyox are found to be higher than the corresponding value for pure water; the value for 50 ppm is the highest (being of the order of 1% higher). This shows that the maximum lowering of the point of maximum density of water occurs at a specific concentration of the solute.

To clear up this point more specifically, further experiments are carried out with 0, 25, 200, 300 and 500 ppm polyox (by weight). The experimental graphs for 0, 200, 300 and 500 ppm are shown in
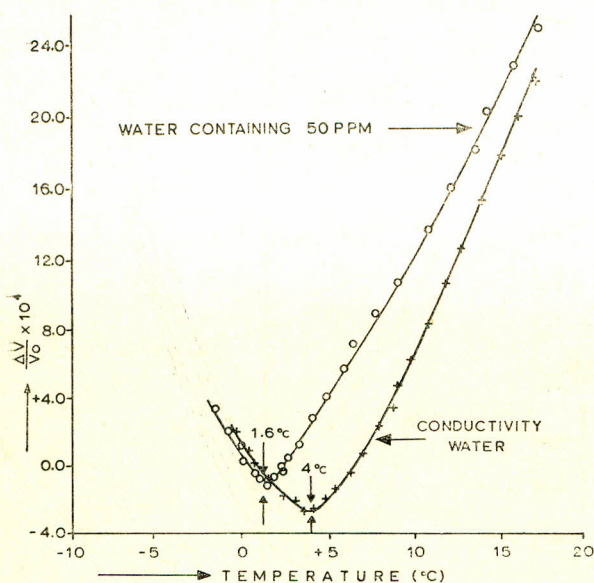
Fig. 2.—Graphs showing the experimental values of ($\Delta V \times 10^4/V_o$) reproduced from earlier communication. Hollow circles represent the graph for water containing 50 ppm polyox, and crosses represent the graph for pure water.

Fig. 3a.—Experimental results ($\Delta V \times 10^4/V_o$) for 0, 50, 75 and 100 ppm polyox (mol wt 4×10^6) plotted separately with solid circles, crosses, hollow circles and triangles respectively.

Fig. 3b. The graphs of Fig. 3b show that the point of maximum density (which is at 4°C for water) is shifted slowly towards higher temperatures with the increase of concentration of polyox above 100 ppm. This is in agreement with the results of Fig. 3a.

Results with Water Containing 0 *to* 400 *ppm Polyox (mol wt* 6,000,000)*:*

At this stage, it is considered essential to extend the experiments to polymer (polyoxyethylene) of different molecular weight. Similar experiments are, therefore, carried out with water containing 0 to 400 ppm polyox of molecular weight 6,000,000.

The first series of experiments are carried out with 0, 15, 25, 50 ppm polyox in the temperature range $-2°$ to 15°C, and the respective experimental results are plotted in Fig. 4a. It is at once seen from the graphs of Fig. 4a. that the point of maximum density of water is again lowered down to the same temperature i.e. 1.7°C, but at 25 ppm polyox in this case, while for 15 and 50 ppm it is at 3.5°C and 4.2°C respectively. This shows that with similar polymer of higher molecular weight, the maximum lowering of the point of maximum density of water occurs at lower concentration of polyox (with increase of density of about 1%). Experimental graphs for higher concentrations (100, 200, 300, and 400 ppm) in Fig. 4b show the slow shifting of the point of maximum density of water occurs towards the higher temperature, in agreement with the results to Fig. 3a and 3b.
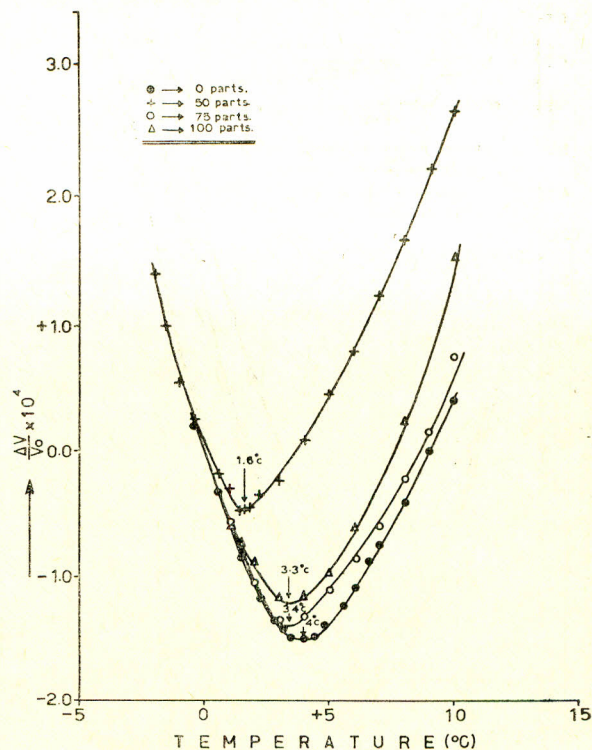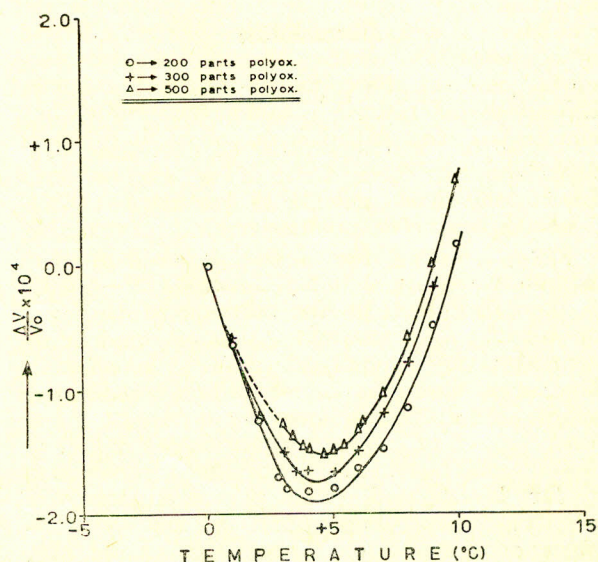

Fig. 3b.—Experimental values of ($\Delta V \times 10^4/V_o$) for 200 300 and 500 ppm polyox (mol wt 4×10^6) plotted separately with hollow circles, crosses and triangles respectively.
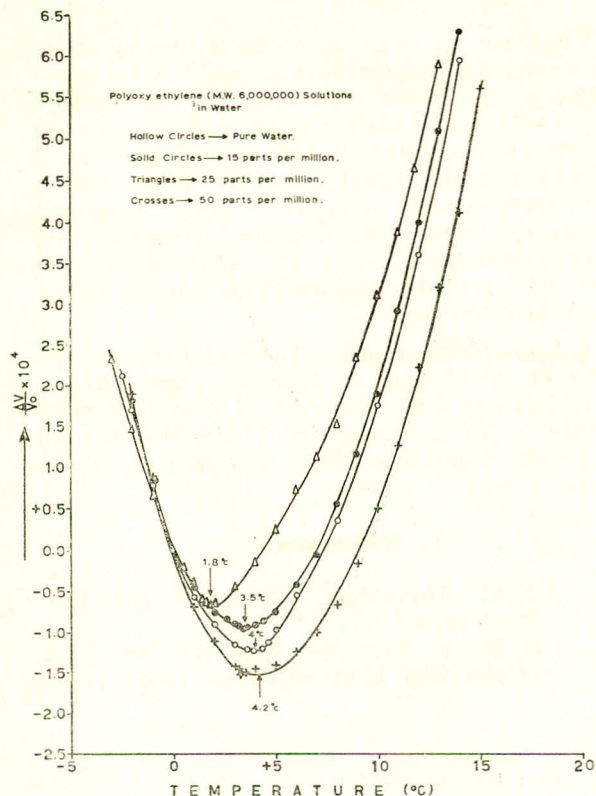
Polyoxy ethylene (M.W. 6,000,000) Solutions in Water.

Hollow Circles → Pure Water.
Solid Circles → 15 parts per million.
Triangles → 25 parts per million.
Crosses → 50 parts per million.

Fig. 4a.—Graphs showing the experimental values of ($\triangle V \times 10^4/V_o$) for 0, 15, 25 and 50 ppm polyox (mol wt 6×10^6). Hollow circles, solid circles, triangles and crosses represent for 0, 15, 25 and 50 ppm respectively.

Discussion

The experimental results of Fig. 2, 3a, 3b, 4a and 4b clearly show that there occurs a definite transition of the temperature of maximum density of water by the addition of very small quantities of long-chain polymer polyoxyethylene, and these temperatures are plotted against polyox conc. in Fig. 5. The greatest lowering of the point of maximum density is to 1.7°C (i.e. $\Delta T = -3.3$°C) in both the cases, by the addition of 50 ppm by weight polyox (mol wt 4,000,000) and by 25 ppm (by weight) polyox (mol wt 6,000,000). This means that with polymer of higher molecular weight the maximum lowering occurs at lower concentration of polymer, as also shown in Fig. 5; this is at least true in the case of these two polymers so far investigated (vide polyoxyethylene) of mol wt 4,000,000 (Fig. 3a and 3b) and polyoxyethylene of mol wt 6,000,000 (Fig. 4a and 4b). It is at once seen from the graph of Fig. 5 that there is a sharp drop in going from pure water to 40 ± 10 ppm polyox (mol wt 4 to 6,000,000) and a sharp
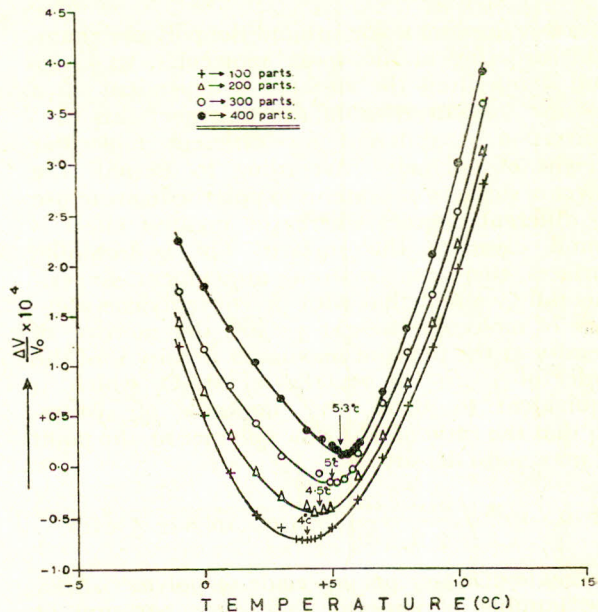

+ → 100 parts.
△ → 200 parts.
O → 300 parts.
● → 400 parts.

Fig. 4b.—Graphs showing the experimental results ($\triangle V \times 10^4/V_o$) for 100, 200, 300, and 400 ppm polyox (mol wt 6×10^6) plotted with crosses, triangles, hollow circles and solid circles respectively.
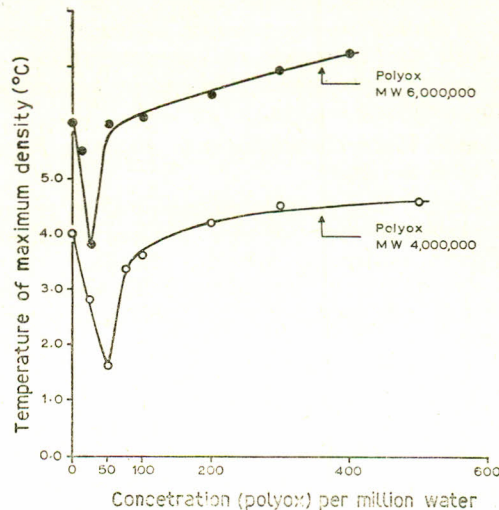

Fig. 5.—Graphs showing the temperatures of maximum density against the concentration of polyox. Hollow circles represent the graph for polymer of molecular weight 4×10^6, and the solid circles represent the graph for polymer of molecular weight 6×10^6.

rise thereafter upto 75–100 ppm. This change becomes progressively slower after 75–100 ppm and the curve finally becomes almost horizontal between 300 and 500 ppm.

From these observations, it seems that the water molecules are able to arrange themselves in an orderly way around the polymer molecules, pre-

sumably forming a skin around the polymer chain. This ordering of the water molecules, its range and depth from the surface, is dependent on a specific concentration of the polymer; this concentration is different for different molecular weight of polymer. According to Bernal[2] the effect of surfaces on water is to polarise its structure to different degrees where the greatest effect is found close to the surface. On hydrophillic surfaces, there can be strong attachment. Experimentally we find that with polyoxyethylene polymer of molecular weight 4×10^6, the increase of density at the point of maximum density is of the order of 9×10^{-4} g per 18g of H_2O, which is equivalent to 6.02×10^{23} molecule of water. So that the ratio of H_2O to polymer at the point of maximum density is

$$6.0 \times 10^{23} \bigg/ \frac{6.0 \times 10^{23}}{4.0 \times 10^6} \times 9.0 \times 10^{-4} \simeq 5 \times 10^9$$

molecule of water per molecule of polymer. Also, the number of molecules of water per unit of polymer $(-CH_2-O-CH_2-) = 5 \times 10^9 / 4.0 \times 10^6 \simeq 55 \times 10^3$.

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Thus, we see that 55,000 molecules of water are attached to a single polymer unit ($-CH_2-O-CH_2-$). Therefore, an estimate of the effective depth of ordering can be made, which comes out to be opproximately $300 A^\circ$ to $400 A^\circ$. It is possible that the actual structural effect stretches out much further than this. Apart from the theoretical interest, this structural effect may well have important biological implications. It is hoped that further exploration on this line will be communicated later.

References

1. A.K.M. Ahsanullah, Pakistan J. Sci. Ind. Res., **12**, 2 (1969).
2. J.D. Bernal, Sym. Soc. Expl. Bio. No. XIX (Cambridge University Press, 1965), p. 17.