Interaction of poly(ethylene oxide) with solvents: 2. Water–poly(ethylene glycol)

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Differential scanning calorimetry (d.s.c.) and water vapour pressure measurement have been used to investigate the poly(ethylene glycol) (PEG) interaction with water. There is a clear evidence for the existence of stable crystalline complexes. One complex clearly contains three moles of water per ether group and exists even at a concentration of 1 part by weight of PEG in 17 parts of water. It melts below 0°C. The vapour pressure results indicate a lower hydrate, which could be a monohydrate, but the evidence from the d.s.c. analysis for this hydrate is less definitive. The formation and stability of these hydrates as a function of molecular weight is further discussed relative to ΔH_{fus} and ΔS_{fus} values determined from d.s.c. curves.

(Keywords: poly(ethylene glycol); poly(ethylene oxide); water; hydrates; d.s.c.; vapour pressure)

INTRODUCTION

This paper follows an earlier paper[1], reporting studies of the interaction of water and solvents with crosslinked poly(ethylene glycol) gels. This paper seeks to obtain further insight into the interaction of water with linear homopolymer poly(ethylene oxide), or synonymously poly(ethylene glycol). The latter term is used for the oligomeric starting materials containing terminal hydroxyls. The former term is used when the hydroxyls have been reacted and the unit is an integral part of a polymer network.

Poly(ethylene glycol) (PEG) is a synthetic molecule of industrial importance and has been extensively studied in the solid state as well as in solution. The structure of PEG has been investigated employing various techniques[2–8], such as X-ray, i.r. and Raman spectroscopy. There seems to be the general agreement that PEG crystallizes in a 7_2 helix conformation. Koenig and Angood[5] have shown that on melting the crystal of PEG, the helix structure was destroyed and a liquid containing random coils was obtained. They also showed that PEG in chloroform and methylene chloride solutions showed no spectroscopic evidence of any significant presence of a helix. Instead the polymer exists primarily in the random coil form. However, in contrast to the melt, the aqueous solution of PEG showed the retention of the polymer in the helix form.

Liu and Parsons[9] have studied the segmental environments of PEG in aqueous solution and suggested that each ethylene oxide unit in the PEG chain, requires three molecules of water to form a hydrated complex. Maxfield and Shepherd[10] have also studied PEG in different states. They proposed that a PEG molecule forms a hydrogen bonded complex in which three molecules of water are involved with each repeat unit and that this hydrogen bonded complex is destroyed if the solution is taken up above the melting point of the PEG. Boehmke and Heusch[11] have carried out viscometric, calorimetric and melting point studies of surface active agents containing short PEG chains and suggested the presence of strongly associated mono, tri, tetra and hexa hydrates of the PEG unit. Several authors[12–15] have explained the anomalies of the heat of solution and dilution for PEG on the basis of its interaction with water. A review[16] of PEG interactions with water has been published with no mention of specific hydrate states.

Investigations of phase behaviour and water binding in PEG solutions have been carried out by using differential scanning calorimetry (d.s.c.)[17,18] and light microscopy[19,20]. The estimated hydration number was found to be 2.7 for PEG.

If a uniform and narrow molecular sample of PEG forms any specific hydrate, then it must have a specific melting point different from that of pure water or of anhydrous PEG and a vapour pressure showing a constant value typical of equilibrium between hydrate forms. This consideration has led the authors to seek very conclusive evidence for specific hydrates by a study of the d.s.c. of PEG samples containing various amounts of water. Support for conclusions arising from the d.s.c. results has been sought and obtained from the vapour pressure experiments.

EXPERIMENTAL

Seven poly(ethylene glycol) samples having molecular weights (M_w) of 240, 440, 560, 950, 1400, 3700 and 5700 of polydispersity indices between 1.04–1.10 were obtained from Polymer Laboratories Ltd. These samples were dried under vacuum at 65°C for 24 h prior to analysis. To known weights of the dry PEG in 50 ml Quickfit flasks, were added the appropriate amounts of distilled water to give the desired ratio of moles of water per ether oxygen in the PEG. The mixture was maintained in the oven for 6 h at 65°C to obtain thorough mixing. It was then cooled to room temperature and allowed to attain equilibrium for 30 days in the sealed containers. The PEG samples of $M_w > 1400$ containing up to one mole of H_2O per ether

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group appeared as semi solids. These became clear liquids with further addition of H_2O. All other PEG samples of $M_w < 1400$ were clear homogeneous liquids at all dilutions.

D.s.c.

A Dupont Model 910 differential scanning calorimeter coupled to a 950 thermal analyser was employed for all the melting measurements. Five to twenty mg of the mixture was transferred to an aluminium sample pan for holding liquid samples. The pan was then hermetically sealed to prevent the water loss, cooled to −80°C, using liquid nitrogen, then heated at a rate of 10°C min^{-1} up to 80°C. The area under the melting peak was measured with a planimeter. Where crystalline melting points and glass transition temperatures are quoted these refer to the intersection with the horizontal (temperature) axis of the tangent to the increasing side of the melting peak, at the inflexion point. Where d.s.c. curves are compared (*Figures 1, 2* and *6*) peak minima are discussed. The heats of fusion (ΔH_{fus}) of hydrate complexes relative to pure indium metal (100% crystalline) were determined from the area of d.s.c. melting endotherms by the peak area method[21,22]. Because location and shape of the endotherm may change considerably[23] on multiple scans of the same sample in all d.s.c. measurements, all samples (in duplicate) were quenched in liquid nitrogen to −100°C, heated at 10°C min^{-1} to 100°C. After a run each sample was discarded.

Vapour pressure measurements

PEG/water mixtures, containing 0.5–5 moles of water per ether group, were prepared and equilibrated by the method employed for the samples used in the d.s.c. experiments to achieve homogeneous mixtures.

An accurately weighed amount of PEG/water mixture was then transferred into a round bottom flask. The mixture was frozen and the flask was attached to the vacuum line equipped with a manometer. After evacuation the flask was removed from the liquid nitrogen trap and eventually submerged in a water bath thermostatically controlled at the required temperature. The change in the manometer reading was taken at the partial vapour pressure of the associated water. Because slight differences in subsequent readings of this vapour pressure were observed in these studies, a large magnification in pressure readings was achieved by adjusting the manometer at an inclined angle of 18.5° to the horizontal. This inclination enabled a magnification of 3, which was realized for any displacement of the mercury column. All readings were obtained by the use of a magnifying glass and it was found necessary to allow for an error of ±0.02 cm in each reading. This gave a cumulative error of 0.126 mm Hg.

RESULTS

The d.s.c. curve of PEG 3700 in 6 moles of water (based on one ethylene oxide monomer unit) is shown in *Figure 1*. It indicates a glass rubber transition (T_g) at −67°C and an exothermic peak preceding the melting endotherm. This exothermic peak is due to the cold crystallization[24] and appears at −41°C. In all subsequent illustrations, this exotherm is not present because the samples were frozen, then held isothermally for 30 min at the cold crystallizing temperature. *Figure 1* also shows the presence of two melting endotherms, one at −8°C and another at 2°C, thus indicating the presence of two types of crystalline water. The d.s.c. curves of pure water, pure anhydrous PEG 5700 and for PEG–water mixtures with different water content are compared in *Figure 2*. It is clear that pure water ($T_m = 0$°C) and pure PEG 5700 ($T_m = 57$°C) gave endotherm minima at 3°C and 62°C respectively, caused by melting of the crystals. At 1 mole of water per ether group of PEG 5700 (*Figure 2*, curve 2) a new and characteristic peak appeared at 23°C, while the melting endotherm minima of the PEG 5700 is depressed to 41°C from 62°C. At 2 moles, another new and most characteristic peak appears at −10°C, while the peak at 41°C (crystalline melt of PEG) has disappeared. Further the addition of 3 moles of water to PEG 5700 (*Figure 2*, curve 4) yielded a single peak at −10°C, thus suggesting the melting of a trihydrate. Beyond 3 moles of water another peak at 0°C appears which, on further dilution, shifts toward the endothermic minimum value of melting of pure ice as indicated in *Figure 2*, curve 5. The stability of the postulated trihydrate (peak at −10°C) was further evaluated quantitatively by plotting the area (cm^2) under the endothermic peak, as a function of moles of water incorporated into PEG 5700 (*Figure 3*). It is significant that the area increases extremely rapidly between 2 and 3 moles of water, and remains fairly constant even after 42 moles of water were added. Above 3 moles of water the extra peak of free water appears and overlaps the trihydrate peak making the precise determination of its area rather inaccurate.

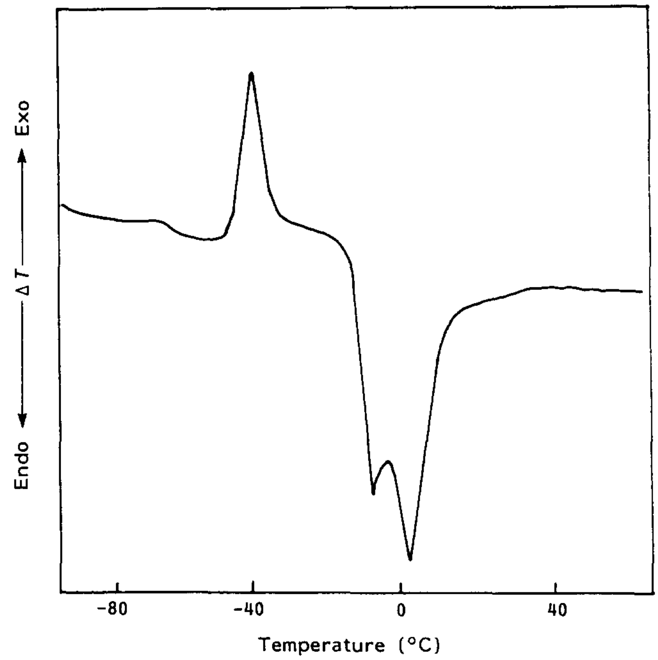

Figure 1 D.s.c. curve for PEG 3700 in six moles of water per ether group. Scan rate 10°C/min

The effect of water on the glass transition (T_g) and the melting temperature (T_m) in the PEG–water system is of interest because if water, as has been shown above, forms specific hydrates through hydrogen bonding, then this effect should be reflected on the physical properties[25] such as T_g and T_m.

Figure 4 shows the variation of T_g as a function of moles of water per ether group present in PEG 5700. It is obvious from the curve that the T_g drops to −73.5°C on addition of 1 mole H_2O from −49.5°C T_g of pure PEG

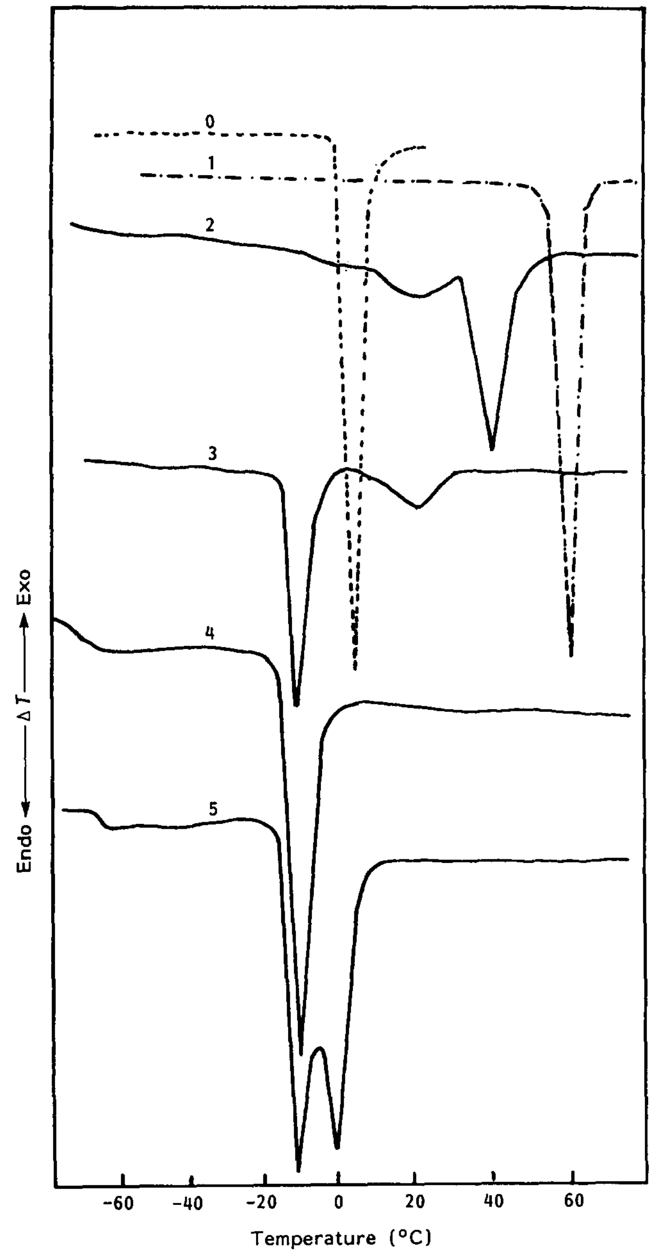

Figure 2 D.s.c. curve for PEG 5700 in presence of various amounts of water per ether group. Scan rate 10°C/min. Curve 0, pure water; curve 1, pure PEG; curve 2, 1 mole water; curve 3, 2 moles water; curve 4, 3 moles water; curve 5, 5 moles water

5700. After that the T_g rises and levels off with further addition of water up to 3 moles per ether group when a trihydrate is formed. Beyond the addition of 3 moles of water, the T_g rises and levels after 6 moles of water have been added. The PEG complexes with one and three moles of water added to dry polymer per ether group, were obtained and the melting temperatures (T_m) were determined from d.s.c. experiments. The values of T_m of hydrate complexes are plotted as a function of the molecular weight of PEG (*Figure 5*). A common trend in the samples studied, which is clearly seen from *Figure 5*, is the increase of T_m with the increase of molecular weight of PEG. The second discernible feature is the higher T_m for mixtures containing one mole of water per ether group as compared with that of trihydrate, e.g. PEG 5700 with one mole of water per ether group melts at +16°C while its trihydrate melts at −16°C.

In order to have a better understanding of the effect of chain length on the hydration of PEG further studies were carried out on PEG of different molecular weights (diluted to various concentrations). In *Figure 6*, on the addition of 5 moles of water to the PEG 440 and 560, the trihydrate peak initially present at 3 moles disappeared, but the trihydrate of PEG 950 was not affected by the dilution. Further, the stoichiometric amounts of water (1 mole and 3 moles) were added to the PEG of various molecular weights. The ΔH_{fus} for mono and trihydrate calculated from the respective peak areas is plotted as a function of the molecular weight of the PEG in *Figure 7*. It is clear that the formation of the lower hydrate starts around 440. From 950 it starts drifting to a lower magnitude as the molecular weight increases. This decrease was found to be due to the changing equilibrium of the PEG solutions of high molecular weight. There were peaks for anhydrous crystalline PEG present in these latter materials. It is shown in *Figure 7* that the trihydrate formation starts around 440 and reaches its highest and roughly constant value around and above PEG 1400.

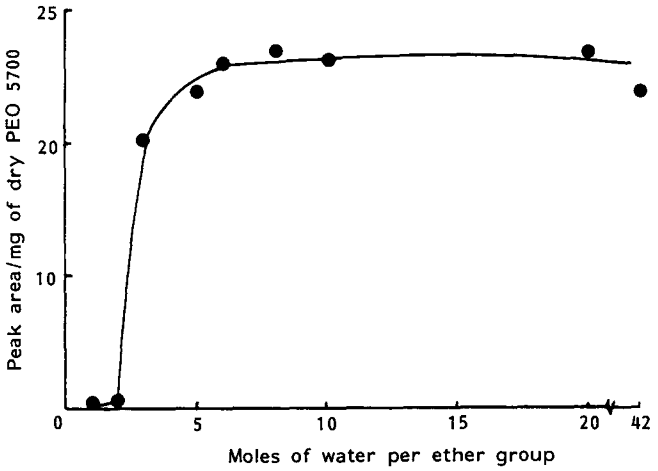

Figure 3 D.s.c. peak area of trihydrate *versus* moles of water per ether group in PEG 5700

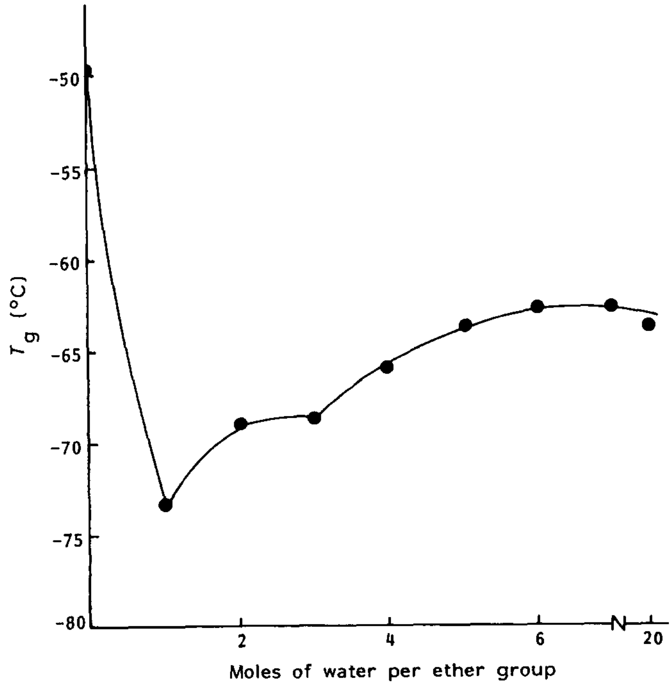

Figure 4 T_g variation with moles of water per ether group in PEG 5700

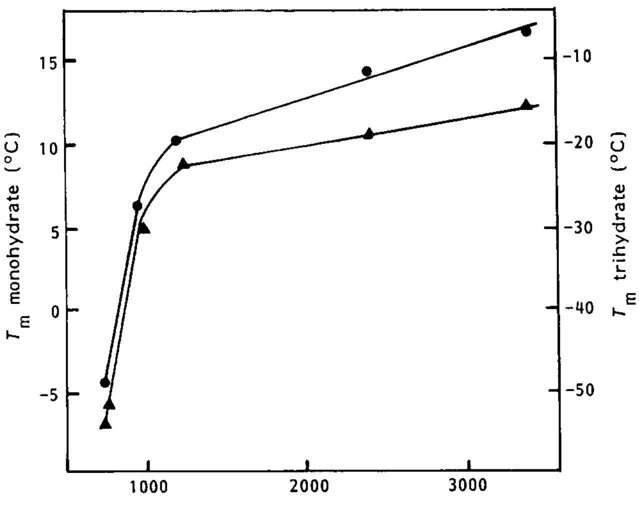

Figure 5 T_m *versus MW* of PEG. ●——, monohydrate; ▲——, trihydrate

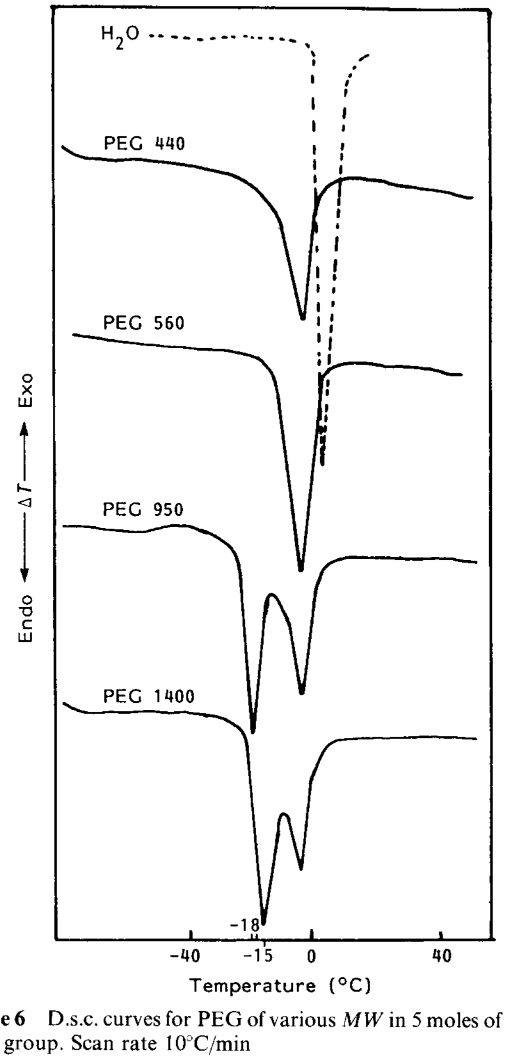

Figure 6 D.s.c. curves for PEG of various *MW* in 5 moles of water per ether group. Scan rate 10°C/min

From the T_m and ΔH_{fus} values, the change in entropy of fusion (ΔS_{fus}) were calculated as per mole of hydrate subunit. These values are depicted in *Figure 7*. The ΔS_{fus} values for trihydrates are higher than those for lower hydrates. It is also clear from *Figure 7* that ΔS_{fus} of the lower hydrate decreases with increase of molecular weight of PEG, whereas an opposing trend is observed in the case of trihydrate.

In an attempt to further characterize the hydrate complexes, the vapour pressure of the PEG 5700 containing varying amounts of water at three different temperatures, has been evaluated. Three plots at 0, 17.5 and 24.5°C are displayed in *Figure 8*. These vapour pressure values are regarded as the partial vapour pressure of the associated water or the reduced vapour pressure of water due to its chemical association with the polymer. Typically the results obtained at 0°C indicate that the process of hydration may be followed by passing from left to right. The first addition of 0.5 moles of water yields a vapour pressure of 2.44 mm Hg and remains constant as long as there is less than 1 mole of H_2O/ether group. When this point is reached, the vapour pressure increases steadily up to the addition of 2 moles of water per ether group. It then stays constant at a 3.3 mm Hg where it remains until the addition of 3 moles of water. Beyond this, the vapour pressure rises and approaches the value obtained for pure water and remains constant.

DISCUSSION

Water usually acts as plasticizer[26] when present in hydrophilic polymers and T_g values decrease with increasing water contents. This phenomenon in the PEG–water systems is only observed up to 1 mol H_2O/ether group. Beyond this a rise in T_g is observed, as in *Figure 4*. The addition of water to PEG increases the order[27–29], but the effect on T_g would depend on the specific structures produced by random mixing and/or by specific complex formation as reported in this paper. These

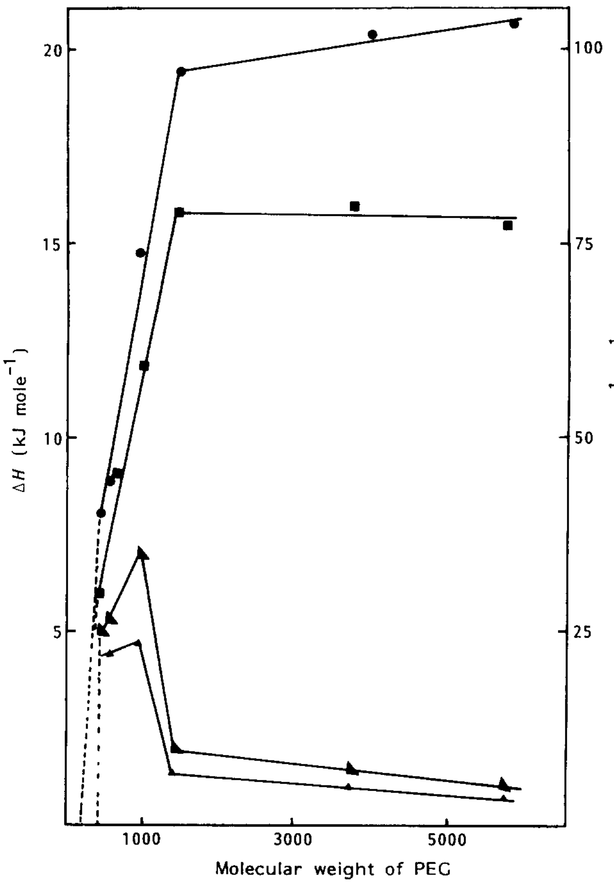

Figure 7 Thermodynamic parameters of mono and trihydrate complexes. ●——, ΔH_{fus} trihydrate; ■——, ΔS_{fus} trihydrate; ▴——, ΔH_{fus} monohydrate; ▲——, ΔS_{fus} monohydrate

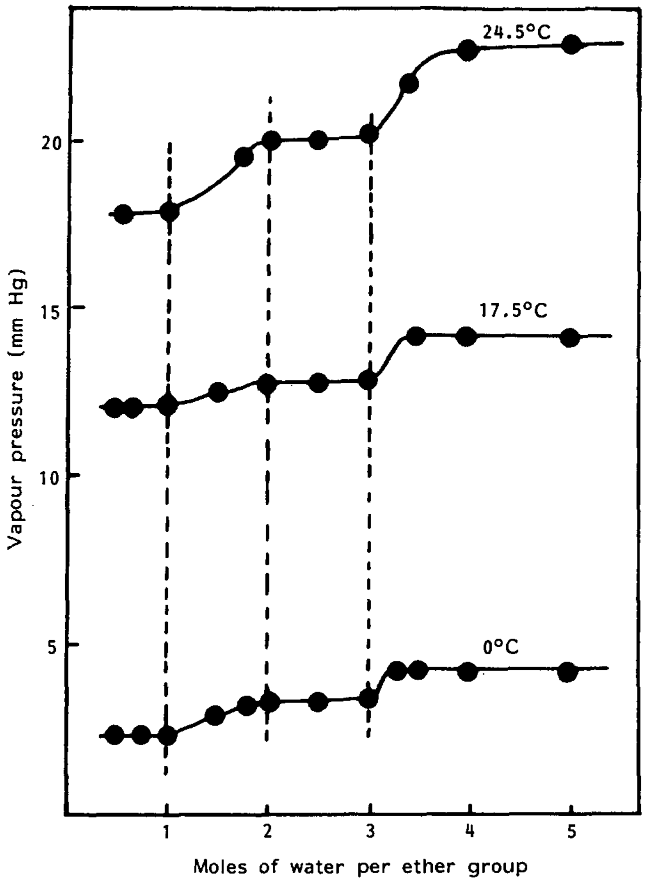

Figure 8 Vapour pressure *versus* moles of water per ether group in PEG 5700 at different temperatures

specific molecular structures are at present unknown. The T_g increased in mixtures with increased levels of water from ratios of 1:1 to 6:1 H_2O:–CH_2CH_2O–. Water is acting as an antiplasticizer rather than a plasticizer in these compositions.

The d.s.c. curve of PEG in aqueous solutions provides some insight into the interaction of the polymer with water. The main factors which lead to the formation of various complexes are the hydrogen bond formation between the oxygen atom of the PEG and the hydrogen atom of water and the structural modification (the iceberg formation)[30] of water around the hydrocarbon portion of the PEG. There is a general agreement[9,13,31,32] that the iceberg formation around the –CH_2CH_2O– chain is somewhat suppressed by the hydrogen bond formation between ether oxygen atoms and water molecules.

In *Figure 2* it is shown that each monomer repeat unit of the PEG 5700 associates with approximately 1 mole of water to form a possible monohydrate in the hydrogen bonding process. This is destroyed when 3 moles of water were added to yield a more stable complex at this temperature. The more stable complex survived considerable further dilution as demonstrated in *Figure 3*. The possible monohydrate melts at a higher temperature than the trihydrate (*Figure 5*).

The melting temperature and the enthalpy of fusion obtained from the d.s.c. endotherms can be used to calculate and compare the entropy change on fusion for the assumed monohydrate and trihydrate. The ΔS_{fus} values for the 'monohydrates' are considerably lower as compared to the corresponding values for trihydrate (*Figure 7*), e.g. for PEG 5700 ΔS_{fus} of monohydrate is 0.39 J mol^{-1} K^{-1} and for PEG 5700 ΔS_{fus} of trihydrate is 75.2 kJ mol^{-1} K^{-1}. This implies that the 'monohydrate' is a stiffer, more rigid species in the melt than the trihydrate if roughly similar proportions of crystalline to amorphous are present in each.

The formation of monohydrate is consistent with the proposal by Boehmke *et al.*[11], who also suggested the existence of other hydrates such as tri, tetra and hexa. Contrary to Rosch's[32] suggestion of dihydrate, *Figure 2* does not show an endotherm for such a complex. There is a body of opinion that PEG in aqueous solution exists as helix[5,9,10] characteristic of the solid PEG[2–8], although the nature of the helix in aqueous solution has only been described in vague terms in contrast with the solid state[5,9,10]. It is shown in *Figure 2* that monohydrate exists only up to 2 moles of water present while the trihydrate which only forms from this level of water remains stable even up to 42 moles of water (*Figure 3*). However, the trihydrates of PEG 440 and 560 decompose after 5 moles of water are added to the PEG as shown in *Figure 6*.

It can also be seen in *Figure 6* that the trihydrate complex of PEG 950 survives further dilution. *Figure 7* demonstrates that the trihydrate starts to form at PEG 440 but at around 1500 the rate of change of ΔH_{fus} with molecular weight undergoes a marked change. This observation is compatible with the idea that in aqueous solutions PEG of adequate chain length can retain some of its solid crystalline characteristic as a helix[2–8].

The PEG 440 and 560 with 10 and 13 monomer units, on the addition of 3 moles of water, crystallize as trihydrate, but this structure is shown to be destroyed on further dilution (*Figure 6*). The complex only becomes stable to dilution between 14 and 22 monomer units in the PEG chain and both the T_m (*Figure 5*) and ΔH_{fus} (*Figure 7*) indicate the thermodynamic properties of the trihydrate complexes are changing rapidly up to a molecular weight of 1400 (32 units of –CH_2CH_2O–) when the slope of the plots sharply decrease. In attempting to construct molecular models of helical trihydrates of poly(ethylene oxide) it is found that structures containing a helix comprising a specific number of –CH_2CH_2O– units per repeating loop are particularly readily constructed. This will be reported in a future communication as will the fact that the association of poly(ethylene oxide) with three moles of water per –CH_2CH_2O– unit is exothermic.

The negative enthalpy change provides the driving force for the formation of the trihydrate. Whatever the precise molecular structure of the trihydrate, it is clear that there are two distinct changes discussed above which occur with increasing molecular weight of the poly(ethylene oxide). If the literature evidence for helical structure of the complex is accepted then the changes can be qualitatively explained in terms of the size of loop and the number of loops in a helix required to form a stable structure. Clearly at least two to four loops are required to generate a structure containing enough water to correspond in composition to a trihydrate and to retain its helical configuration. In fact the lowest molecular weight of PEG showing d.s.c. melting of a trihydrate in the presence of considerably more than 3 moles of water per –CH_2CH_2O– was 950 corresponding to 22 monomer units. This represents 6 loops of a 7_2 helix or fewer of a larger loop. The second change would be expected when the length to diameter ratio of the helix reaches a value where the stacking of the molecules in the crystal is modified and is observed at a PEG *MW* of 1400 or 32 units. In postulating trihydrate structures it is necessary to accommodate the third water molecule as a bridge between water molecules hydrogen bonded to the ether groups. It is only possible to accommodate two such H-bonded water molecules attached directly to the ether groups.

Figure 8 shows that essentially all the added water up to 1 mole/ether group complexes with PEG and forms a 'monohydrate'. As a result a plateau in the vapour pressure plot between 0.5 to approximately 1 mole of H_2O is obtained. With further addition of water the vapour pressure rises and a trihydrate forms on addition of water >2 moles per ether group. Hence a second plateau between 2–3 moles of H_2O/ether group; the vapour pressure approaches to the values obtained for pure water at the respective temperatures and remains constant with further dilution. Typically the vapour pressure at 17.5°C and 3.5 moles of H_2O was 14.15 mm Hg, which is the vapour pressure of water. The interpretation of the plateau as mono and trihydrate is analogous to the application of phase rule often applied to salt hydrates. It is known[33] that the vapour pressure of a system at equilibrium (e.g. pure solvent) at a given temperature continuously changes with the introduction of a solute but when specific complexes are formed a constant vapour pressure is obtained for part of the composition/vapour pressure plot. A small gradual rise in vapour pressure in the region of 1–2 moles per ether group (*Figure 8*) is not consistent with the salt hydrate plot[33]. The presence of a dihydrate in PEG/H_2O system has been postulated by other authors[11]. However d.s.c. and vapour pressure experiments do not provide supporting evidence. The d.s.c. and vapour pressure experiments strongly support the presence of a trihydrate complex when PEG is brought in contact with water and also point to a lower complex which is most probably a monohydrate.

CONCLUSIONS

The above results present clear evidence for the existence of stable crystalline complexes of polyethylene glycols with three moles of water and also with lower molar ratios. The trihydrate is very stable and exists even at concentrations of 1 part by weight of PEG in 17 parts of water at around −16°C but has been clearly demonstrated by its vapour pressure to be stable to at least up to 24.5°C. Because the specific hydrates of poly(ethylene glycol) only form at PEG molecular weight values in excess of 440 it is clear that in studies of the interaction of water with the polymer, the molecular weights and their distributions should be known and stated. The molecular weight range up to around 1500 provides rapidly changing interaction and caution would be advisable in making conclusions on complex formation from this region in the absence of such molecular weight data. Because many surface active agents based on poly(ethylene oxide) contain chains in this critical range it may well be that the multiplicity of hydrates reported for such materials may be explained in terms of their ability or otherwise to form the hydrate structures.

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