Aqueous Solutions of Polypropylene Oxide: Unusual Solution Behaviour

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Density, calorimetric and rheological measurements for poly(propylene oxide)–water solutions, which are completely miscible over the total concentration range, indicate that, in dilute solutions of the polymer in water, interactions between the polymer and water are very similar to those seen with corresponding concentrations of short chain alcohols in water and also suggest that specific interactions between the polymer and water occur in dilute solutions of water in the polymer.

Block copolymers of the structure, polyethylene oxide–polypropylene oxide–polyethylene oxide (PEO–PPO–PEO), the Pluronics, are reported to exhibit strong surface active behaviour, including micelle formation.[1–4] The factor of strongest influence in promoting micelle formation is reported to be the presence of the central block of the hydrophobic polymer PPO.[4] This is notwithstanding the fact that the lower molar mass examples of PPO (up to *ca.* 1000) are known to be water soluble, albeit exhibiting lower critical demixing behaviour. Little quantitative evidence however exists in the literature detailing the aqueous solution behaviour of PPO, apart from the early work of Malcolm and Rowlinson.[5]

We carried out a more rigorous investigation of the aqueous solution behaviour of PPO. We report here the preliminary results, obtained from measurements of the viscoelasticity of PPO–water solutions, high precision measurements of their density and microcalorimetric measurements of their heats of dilution in water at 20 °C.

The sample of polypropylene oxide, purchased from Fluka AG Chemie, with a quoted molar mass of 400, gave a single peak by gel permeation chromatography and was subject to drying at 80 °C under vacuum for 24 h before use. Density measurements were made using previously reported techniques[6] and had a precision of 1×10^{-4} kg m^{-3}; the microcalorimetric measurements, also using previously reported procedures,[7] had a precision of 1×10^{-7} J. Rheological measurements were obtained using an Anton Paar OCR-D Oscillating Capillary Rheometer.

The excess partial specific volumes[8] of PPO ($\bar{V}_2^E$) and water ($\bar{V}_1^E$) are shown in Fig. 1, for both PPO and water, as a function of weight fraction PPO concentration. The plot for PPO shows that a minimum occurs at approximately 0.15 weight fraction, similar, in both position and magnitude, to that seen in ethanol–water mixtures.[9] Such behaviour suggests that the interaction of PPO with the water is of a similar nature and that hydrophobic hydration of the polymer is an important factor in its dilute solution behaviour, which has maximum effect at around this weight fraction. The plot for water shows markedly larger negative values above weight fraction 0.8, indicating that, in this region of lower water contents, considerable changes are occurring in the interaction between water and PPO. In this case also the negative excess value at infinite dilution of the water is comparable to that seen for water in ethanol solutions,[10] which has been attributed to extensive hydrogen bonding of water molecules to the alcohol; this evidence suggests that a similar pattern pertains for water in PPO.

The pair interaction coefficient at infinite dilution,[8] V_{22}, was determined to be -0.336 m^3 kg^{-1} for PPO, again highlighting the importance of hydrophobic hydration in the dilute solution behaviour of the PPO,[11] the positive value of 1.28 for the corresponding term for water in PPO at infinite dilution, V_{11}, supports the conclusion that hydrogen bonding between PPO and water is an important feature of this solution behaviour.

Comparison of Fig. 1 with Fig. 2 shows that discontinuities occur in the change in partial specific enthalpy of PPO in water, $\Delta H/(w_f - w_i)$, where ΔH is the heat of dilution and w_f and w_i are the final and initial weight fractions of PPO, at those concentrations that correspond to the changes observed in the excess partial specific volume data. The maximum value of the enthalpy term coincides with the minimum in the specific excess volume of PPO, behaviour which, yet again, closely resembles that of ethanol–water mixtures, whilst the discontinuity in the enthalpy term, at 0.75 weight fraction, is coincident with the region where the excess partial specific volume of water PPO is becoming much more negative. The enthalpy data also shows that at very low water contents there is a strong curvature in the plot of Fig. 2, suggesting that in this region a different interaction is occurring.

The positive value of the pair interaction coefficient, h_{22}, 121 J g^{-1}, obtained by extrapolation of the data in Fig. 2 to infinite dilution of PPO, is further confirmation that hydrophobic hydration is an important factor in the aqueous solution behaviour of PPO, controlling the formation of pairs by hydrophobic interaction.[12]

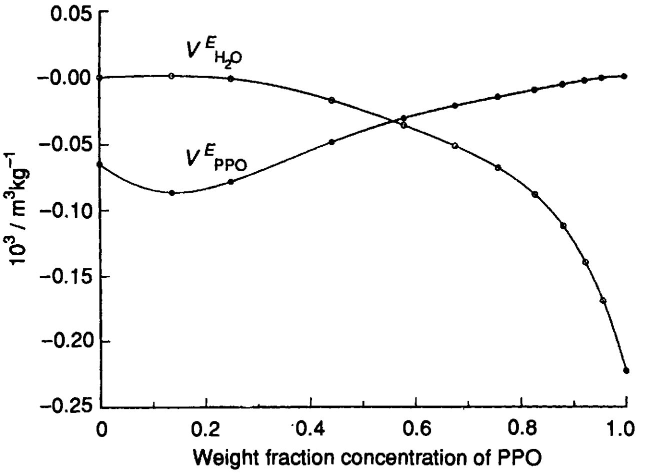

Fig. 1 Excess partial specific volumes, at 20 °C, of polypropylene oxide ($\bar{V}_2^E$) and water ($\bar{V}^{1E}$) as a function of the weight fraction concentration of polypropylene oxide

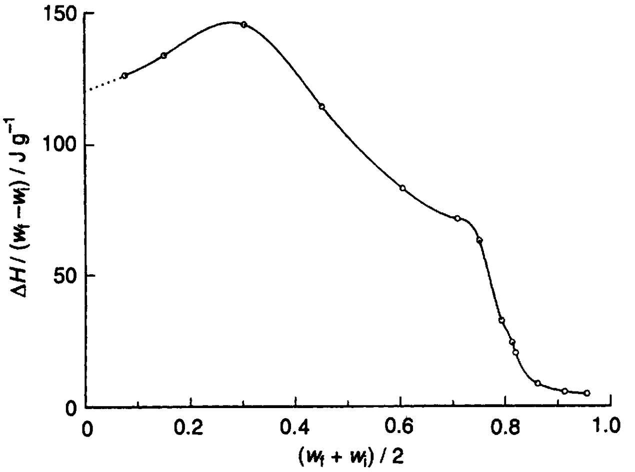

Fig. 2 The difference in partial specific enthalpy, $\Delta H(w_f - w_i)$ in J g^{-1}, at 20 °C, as a function of the mean polypropylene oxide weight fraction concentration $(w_f + w_i)/2$

Fig. 3 illustrates the value of the viscous (η') and elastic (η'') components of the flow behaviour of the PPO–water solutions as a function of weight fraction of PPO; the viscous component of the flow behaviour increases smoothly with increasing PPO content up to 0.75 weight fraction, showing no obvious correlation with the dilute solution behaviour previously discussed. At higher PPO contents the viscous behaviour is an exact mirror of the behaviour of the enthalpic term, a discontinuity occurs at weight fraction 0.75, in agreement with that seen in the enthalpy data, followed by a peak at 0.95 weight fraction, corresponding to the change in the slope of the enthalpy plot. Coincident with the discontinuity in the viscous component behaviour is the appearance of an elastic component in the flow behaviour, which increases rapidly in the magnitude with increasing PPO content to peak at the same PPO content as that for the peak in the viscous component.

This flow behaviour is seen for all rates of applied shear from 0.1 s^{-1} up to 100 s^{-1}, which implies that the interaction between the water and PPO molecules at high weight fractions of PPO must be of a very stable nature.

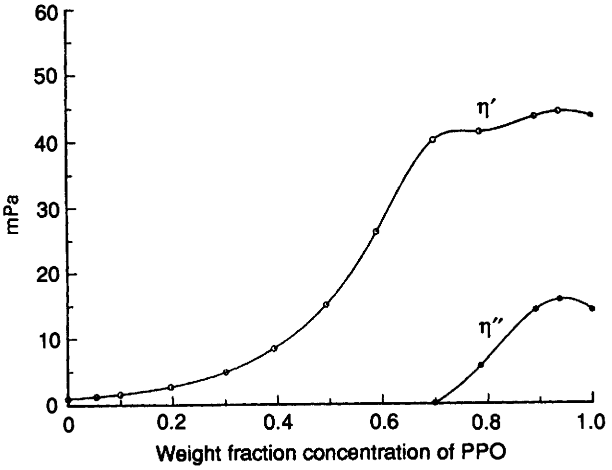

Fig. 3 The viscous (η') and elastic (η'') components of flow in mPa, at 20 °C, of polypropylene oxide–water solutions, as a function of weight fraction polypropylene oxide concentration

The enthalpy data indicate that the differences in the partial specific enthalpies become much less at the higher weight fractions of PPO, being 75 J g^{-1} at weight fraction 0.75 and only 5 J g^{-1} at weight fraction 0.95. These smaller values, compared to those seen in the more dilute solutions again imply that very little change occurs on dilution and confirm that a very stable grouping exists. The evidence from alcohol–water mixtures revealed the importance of hydrogen bonding for higher alcohol content mixtures and the similarities are clear in the case of PPO–water. On this basis the number of water molecules hydrogen bonded per PPO that correspond to the concentrations of 0.75 and 0.95 weight fraction can be calculated, seven and two respectively, which correspond to one water molecule per repeat monomer unit in the first case and one for each end group in the second.

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