Interaction of poly(oxyethylene) with water as a function of molar mass

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Partial base molal volume values obtained from high-precision density measurements, in conjunction with heats of dilution data, derived from flow calorimetry measurements, have been obtained for a series of samples of poly(oxyethylene) (POE) of different molar masses, ranging from 200 to 35 000 Da. The results show that the state of solution of the POE is very much dependent upon the molar mass of the polymer; at low molar masses, pair and triplet interaction coefficients suggest that the hydrophobic interaction controls solution behaviour, while at higher molar masses, a helical conformation appears the most likely explanation.

(Keywords: poly(ethylene oxide); molar mass; partial base molal volume; heat of dilution; pair and triplet interaction coefficients)

INTRODUCTION

The involvement of poly(oxyethylene) (POE) in complex formation with polycarboxylic acids has been extensively studied[1-3]; further, the involvement of such complexes in emulsion polymerization has been reported[4], where a dependence of the size of the polymerized particle upon the molar mass of the POE was apparently observed. Investigations of the solution state of POE itself, however, as a function of molar mass appear to have been relatively few in number, and have yielded conflicting conclusions.

The early investigations by Malcolm and Rowlinson[5] of the heats of dilution of POE samples of different molar mass, over an extended range of concentration at the elevated temperature of 80.3°C, indicated no dependence upon molar mass within the high dilution range and even extending up to 50% w/w concentration, where a maximum in the heat of dilution was observed. Later calorimetric investigations by Kagemoto *et al.*[6], over the molar mass range of 200 to 6×10^5 Da, suggested, however, that a dependence of the heat of dilution upon molar mass does exist, the process becoming more exothermic the lower the molar mass.

Molyneux[7] interpreted the largest value of the heat of dilution from the data of Malcolm and Rowlinson, at 50% w/w and the values in the high dilution region, as an interaction of two moles of water per base mole of POE, both molecules of water being hydrogen bonded to the oxygen of the EO monomer, with no clear indication of any role for hydrophobic hydration possibly associated with the $-CH_2-CH_2-$ region.

Blandemer *et al.*[8] suggested that the POE chain can be accommodated within the hexagonal water structure (ice I_h structure), since the distance between alternate oxygen atoms of POE in a suitable conformation equals the next-nearest-neighbour distance (≈ 0.47 nm) of the water oxygen atoms. Maijgren[9] subsequently observed

that for the helical conformation of POE in the crystalline state, the closest oxygen–oxygen distance (0.288 nm) is similar to that of liquid water at 25°C; the derived structural model incorporated the single polymer chain in a hexagonal water lattice as a modified helix oriented in the *c*-direction of the lattice (perpendicular to the hexagonal layers).

Kjellander and Florin[10] have recently developed a simple statistical model, based upon the use of either the cubic or hexagonal ice lattice, so that when the number of water molecules per monomer unit is 2, one-third of the water molecules are replaced by ether oxygens of the POE chain. Most of the ethylene segments are in a *gauche* conformation, in agreement with infra-red and Raman measurements[11,12]. The natural consequence of this model is that all the ether oxygens point outward to the water, the adjacent methylene groups are surrounded by the natural cavities in the water and the POE molecule adopts a helical conformation with a purely hydrocarbon core. The role that may be attributed to hydrophobic hydration is not clear from the model and, further, it is implicitly assumed that behaviour as a function of chain length is invariant.

In contradiction to the proposals of Molyneux and Kjellander and Florin, Graham and co-workers[13-16], from an extended series of d.s.c. measurements on solutions and cross-linked hydrogels of POE, show that the polymer exists as a trihydrate, which is stable, even at high levels of dilution, but only for molar mass values greater than a critical value of approximately 1500 Da, when the polymer, as a consequence of the hydration, is said to adopt a helical conformation, with the ether oxygens, in this particular case, pointing inwards to a concentric complexed shell of three water molecules per ether group, and presenting a relatively hydrophobic outer surface to the bulk water.

Char, Frank, Gast and Tana[17], using fluorescence techniques, have investigated pyrene end-group-labelled POE in water and methanol/water mixtures, and

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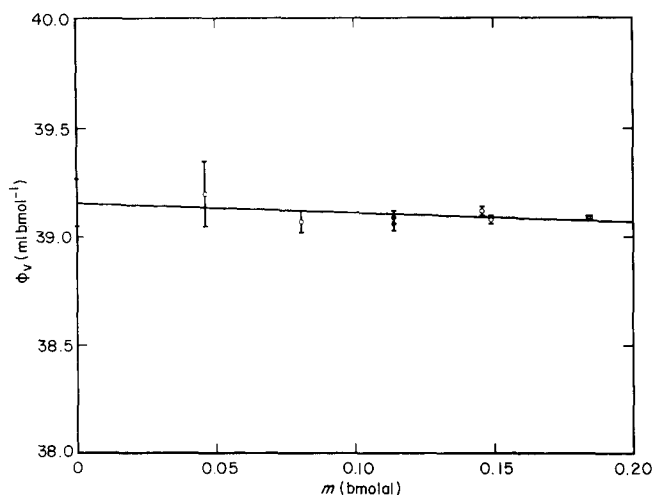
Figure 1 The apparent molal volume, ϕ_v, at 80°C, expressed on a base molal basis, of POE (molar mass 400 Da), as a function of concentration. The error bars in this and all subsequent figures are the 95% confidence limits of the data. $V^0 = 39.16 \pm 0.04$ per base mol

observed that the excimer-to-monomer ratio for low molar mass (4800 Da) was unexpectedly high in aqueous solution, but decreasing with increasing methanol content. The authors attribute this behaviour to cyclization, caused by hydrophobic interaction, but which probably involves the pyrene end-groups.

The situation may be further complicated by the presence of aggregates in the solution. Polik and Burchard[18], using static light-scattering techniques and a POE sample of molar mass 2.0×10^4 Da, observed the presence of both high and low density aggregates. This result appears to have been at least partially confirmed by the dynamic light-scattering studies of Brown[19], who reported the presence of aggregates in a solution of POE, molar mass 2.5×10^4 Da, but not in a solution of molar mass 4×10^3 Da.

As part of an investigation of the importance of the molar mass of POE for its function in complexation with polymeric carboxylic acids, we have examined the heat-of-dilution behaviour of POE as a function of molar mass, together with high-precision density determinations of the apparent molar volume, in order to ascertain what importance, if any, hydrophobic hydration/interaction might have for the solution process.

EXPERIMENTAL

Narrow molar mass fractions of POE, ranging from 200 to 3.5×10^4 Da, were supplied by Merck and used without further purification. Mean molar mass values were taken as those quoted by the manufacturer ($\pm 5\%$), determined using hydroxy end-group phosgenation, which have been confirmed by Michalczyk and Burchard[20], using both vapour pressure and membrane osmometry.

All solutions were made up on a direct weight-to-weight basis, to an accuracy of six significant figures, using water from a high-efficiency distillation system[21].

Density measurements were obtained to a precision of 1.5×10^{-4} kg m^{-3}, using a Paar vibrating cell densimeter, model DMA 02c, thermostatted to better than 1×10^{-3}°C. Microcalorimetric measurements were made with an LKB flow calorimeter, model 2107/121, in the mixing mode, thermostatted to 1×10^{-4}°C,

yielding data with a precision of 1×10^{-6} J when the flow rates of POE solution and water were closely matched.

RESULTS AND DISCUSSION

Apparent molal volumes, ϕ_v, of each molar mass sample of POE, over a range of concentrations, were given by:

$$\phi_V = \frac{(\rho_0 - \rho)}{m\rho_0\rho} + \frac{M}{\rho} \qquad (1)$$

where m is the molality of the solution, M is the molar mass of the solute, ρ is the density of the solution and ρ_0 is the density of the solvent, in this case water. Errors in the determination of the density of the solution and in weighing components must lead to errors in the determined values of ϕ_v, and hence in the values of V^0, the partial molal volume, derived by:

$$\overline{V^0} = \phi_V + m \frac{d\phi_V}{dm} \qquad (2)$$

At infinite dilution the apparent molal volume and the partial molal volume are identical in magnitude, therefore a plot of ϕ_v versus m will yield a value of $\overline{V^0}$ when extrapolated to infinite dilution.

Differentiation of equation (1) with respect to ρ and m allows the magnitude of the combined error in ϕ_v to be assessed. *Figure 1* illustrates a plot of ϕ_v, expressed per base mol, versus m for a sample of POE, molar mass 400 Da, at 80°C, the magnitude of the error for each determination is shown by the error bars; extrapolation of the data to infinite dilution allows determination of V^0 per base mol, within 95% confidence limits, as shown. The data plotted in *Figure 1* show clearly how the error on the apparent base molal volume increases with decreasing concentration, even at this high precision in density measurement, and the necessity of obtaining data over a sufficiently wide spread of concentration, in order to ensure that no concentration-dependent change in molecular volume is occurring, and that an accurate value of the base partial molal volume might be obtained. A similar analysis was performed for the data at each molar mass of POE at the two temperatures, the results are shown in *Figures 2* and *3*, plotted as a logarithmic function of the molar mass of POE.
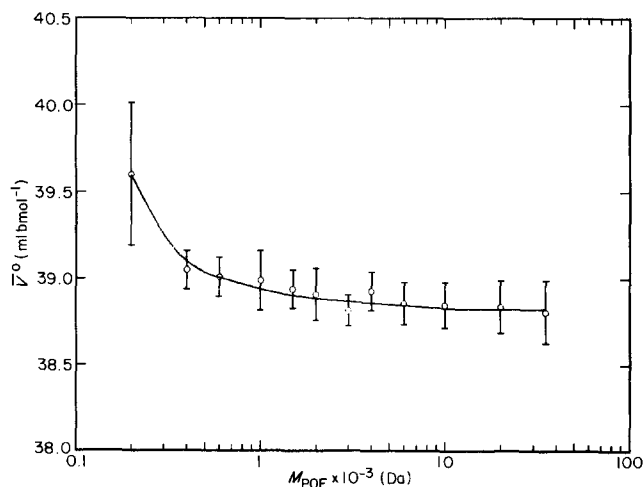
Figure 2 The partial molal volume, V^0, at 80°C, expressed on a base molal basis, of POE, as a function of the molar mass of the polymer, on a logarithmic scale
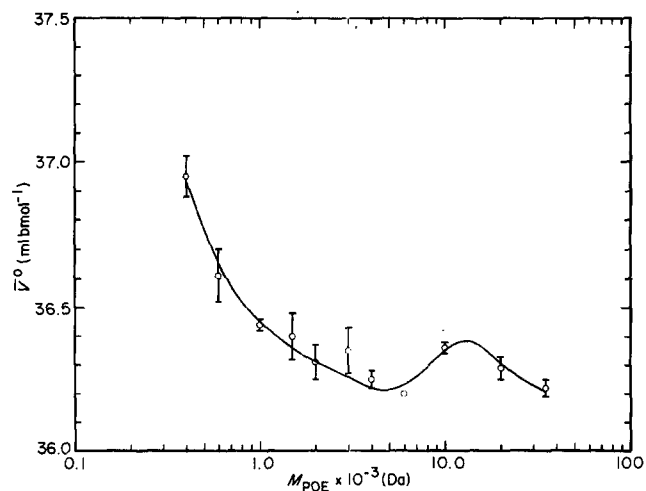
Figure 3 The partial molal volume, V^0, at 10°C, expressed on a base molal basis, of POE, as a function of the molar mass of the polymer, on a logarithmic scale

Comparison of the data in *Figures 2* and *3* shows that, in general terms, a difference in base molal volume of approximately 2.5 ml mol^{-1} exists between the data at 80°C and that at 10°C, presumably reflecting the change in solute–solvent interactions with increase in temperature. The shapes of the two plots appear similar, inasmuch as in both cases the partial molal volume initially decreases rapidly with increasing molar mass, but at higher values of molar mass the two plots appear somewhat different. In the case of the 10°C data a clear minimum is seen, at about 6000 Da, followed by a maximum, whereas with the 80°C data, within the accuracy of the data, no minimum can be seen, and the value of the partial molal volume decreases more slowly with increasing molar mass. The data for the higher molar masses, at both temperatures, fit a linear relationship with excellent correlation coefficients, but the linearity does not extend in either case over the whole range of molar mass. This is seen clearly in the case of the 10°C data, where a minimum is observed, but a deviation from linearity is also seen in the 80°C data, at a molar mass of about 3–4 × 10^3 Da.

The partial molal volume data seem to indicate that, for molar masses less than a critical value, 3–4 × 10^3 Da in the case of the higher temperature and about 6000 Da for the lower, an involvement of some kind with the solvent is quite strong, but decreases with increasing molar mass. The most rapid rate of decrease is observed with the very lowest molar masses and, assuming that the effect is due to a simplistic division between end group $-CH_2OH$ and main chain $-CH_2CH_2O$ groups, it is possible that the decrease in V^0 might be associated with a lessening of the end group effect *vis-à-vis* the main chain contribution. On the basis of this assumption, V^0 for the lower molar masses might be subdivided into the end-group and main-chain contributions according to the following equation:

$$\overline{V^0} = xV_c + 2V_e \qquad (3)$$

where x is the degree of polymerization (DP), V_c is the main-chain contribution and V_e is the end-group contribution. Rearrangement of this equation results in

$$\frac{\overline{V^0}}{x} = V_c + 2\frac{V_e}{x} \qquad (4)$$

Thus a plot of V^0/x, the base molal partial molal volume, *versus* $1/x$ should be a straight line of slope $2V_e$ and intercept V_c. Attempts to fit the data to this equation were not very successful, for either the data at 10° or 80°C, correlation coefficients of 0.983 being obtained. Correlation coefficients of this magnitude cannot be regarded as satisfactory proof of a linear relationship, thus a simplistic division into main-chain and end-group effects does not appear to be the answer. It should be noted, however, that hydrophobic interaction between apolar groups such as $-CH_2-CH_2-$ leads to a decrease in V^0 (ref. 22); it is therefore possible, at least in the case of the lower molar mass examples of POE, that a hydrophobic interaction is occurring.

The enthalpy contribution, χ_H, to the Flory–Huggins free energy, polymer solute–solvent interaction parameter, χ, may be determined from heat of dilution data by:

$$\chi_H = \frac{\Delta H_d}{V_i V_f \Delta n R T} \qquad (5)$$

where ΔH_d is the measured heat of dilution for the addition of Δn moles of water to a solution of initial volume fraction concentration V_i, to produce a solution of final volume fraction concentration V_f. Such heats of dilution were measured, at 15°C and 20°C, over a range of polymer concentrations for each molar mass of POE, and the corresponding value of χ_H determined according to the above relationship; *Figure 4*, illustrating the plot of χ_H against the mean of the volume fraction concentrations for POE, molar mass 2000 Da, at 20°C, is typical of the plots obtained. The error bars for the individual data points represent the 95% confidence limits on the data, from repeated measurements, and extrapolation of the linear relationship to the intercept yields the infinite dilution value, χ_H^0, together with the associated 95% confidence limits. *Figure 5* shows the plot of χ_H^0 against log molar mass of POE at 15°C and 20°C which for corresponding molar masses shows good agreement with the data of Kagemoto *et al.*[6], with a strong dependence on the molar mass. The dependence upon molar mass is similar to that seen with the partial molar volume data, in that the magnitude of χ_H^0 increases with increasing molar mass, up to about 3000 Da.
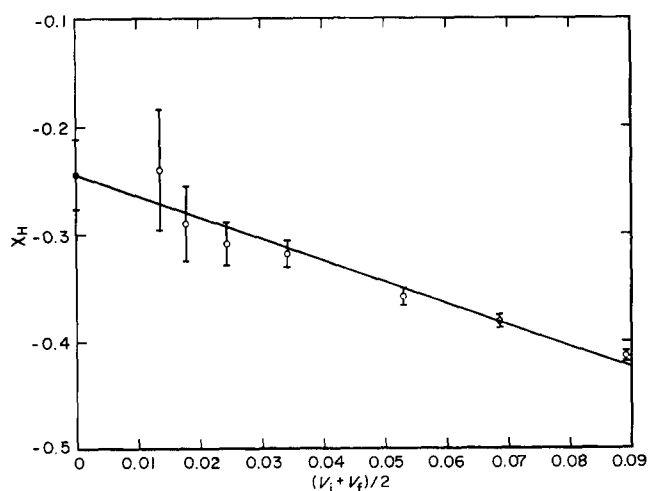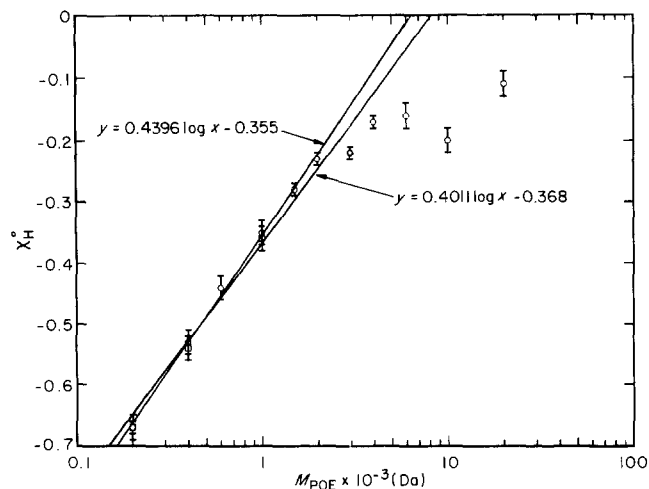

Figure 4 χ_H, the enthalpy contribution to the Flory–Huggins χ parameter, of POE (molar mass 2000 Da) at 20°C, as a function of the mean of the volume fraction initial and final concentrations

Figure 5 χ_H^0, the infinite dilution values of χ_H, at 15°C (O) and 20°C (□), as a function of the molar mass of the polymer, expressed on a logarithmic scale

An increasingly negative value for χ_H^0 has been reported[23] as indicating an increasing hydrophobic involvement in the solute–solute interaction parameter, the solvent effectively becoming 'worse', until eventually precipitation occurs[24]. The limited data obtained at 20°C show greater values than at 10°C, indicating that the solvent is becoming 'worse' with increasing temperature, again a characteristic of a hydrophobic contribution.

The calorimetric data thus seem to confirm that the variation of partial molar volume, seen as a function of molar mass, at least for the lower values, is a result of an increasingly important hydrophobic contribution which arises in conjunction with a decreasing molar mass. If the assumption is made of two contributing components to χ_H^0, as in the case of V^0, and a corresponding linear equation developed:

$$\frac{\chi_H^0}{x} = \chi_c + 2\frac{\chi_e}{x} \qquad (6)$$

it is immediately clear that no linear relationship exists, the lower molar mass data in fact fitting a three-term polynomial extremely well. The calorimetric data therefore confirm the conclusion drawn from the partial molal volume data, that there is no clear distinction into 'end-group' and 'chain' contributions, although a hydrophobic contribution is, in some way, involved.

The McMillan–Mayer theory of solutions[25] allows the formal separation of effects arising from molecular pair, triplet, etc. interactions from those accounted for by solute–solvent interactions; the coefficients characterizing the interactions between like molecules can be obtained from the heat of dilution, ΔH_d, by:

$$\frac{\Delta H_d}{m_f(m_f - m_i)} = h_{xx} + h_{xxx}(m_i + m_f) \qquad (7)$$

where m_i and m_f are the initial and final concentrations, and h_{xx} and h_{xxx} are the pair and triplet interaction coefficients. A plot of the left-hand side of this equation against $(m_i + m_f)$, giving a straight line of slope h_{xxx} and intercept h_{xx}, for the data at 15°C, is shown in *Figure 6* for POE of molar mass 1000 Da, together with the 95% confidence limits of h_{xx} and h_{xxx}. This kind of plot is typical of the data for all the samples of POE and *Figure*

7 illustrates the manner in which the pairwise interaction coefficient h_{xx} varies with molar mass of POE.

Positive values of the pair interaction coefficient have been shown[26] to be indicative of hydrophobic character in the solute–solute interaction, hydrophilic type interactions giving rise to negative pairwise coefficients[27], thus it is clear that the greatest hydrophobic contribution arises with the smallest molar masses, decreasing to a minimum value at molar mass of about 6000 Da, with a discontinuity arising between molar mass of 6000 and 10000 Da. The decrease in magnitude of h_{xx} is accompanied by an increase in the size of h_{xxx}, the triplet interaction coefficient; the ratio of h_{xxx}/h_{xx} is non-existent for POE of molar mass 200 Da, but grows to approximately 40% of the magnitude of h_{xx} for POE of molar mass 6000 Da.

It would appear that the explanation of the solution behaviour of lower molar masses of POE lies in hydrophobic contact grouping of the molecules, which increases from dimers to trimers as the molar mass increases. An abrupt change occurs at a molar mass of about 6000 Da, the pair coefficient increasing and the triplet again falling to zero; this could be due to the longer molecule increasingly being able to adopt a helical structure, possibly in conjunction with aggregation of the
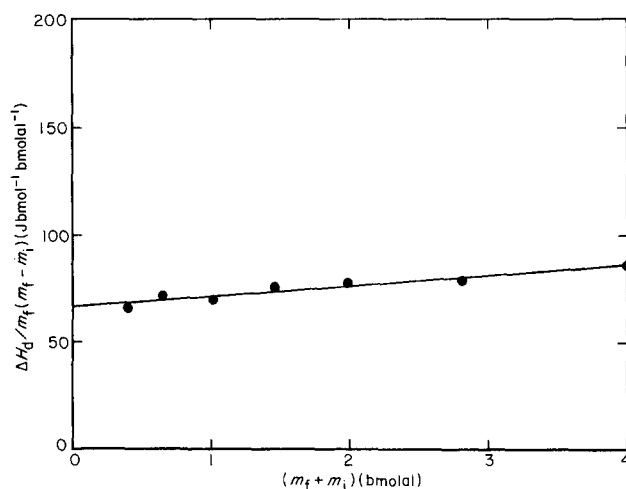
Figure 6 $\Delta H_d/m_f(m_i - m_f)$, at 15°C, as a function of $(m_i + m_f)$, for POE of molar mass 1000 Da. $h_{xx} = 66.7 \pm 1.5$; $h_{xxx} = 4.9 \pm 0.7$
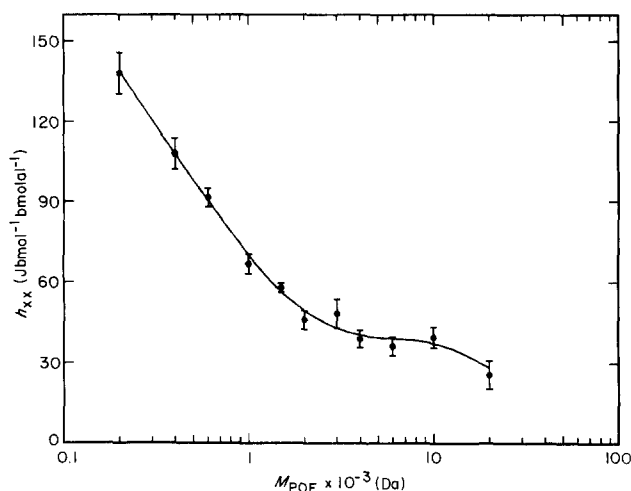
Figure 7 The pairwise interaction coefficients, h_{xx}, as a function of the molar mass of POE, on a logarithmic scale

helices, which may explain the light-scattering results of Brown[19].

It may be recalled that helical structures have been proposed by both Graham[13] and Kjellander and Florin[10], the two helical models being, however, very different in architecture; the data presented here suggest that, for the helical conformation, hydrophobic hydration has been reduced to a minimum which, in conjunction with a higher level of pairwise interaction, suggests that hydrophobic regions have been removed from contact with the surrounding solvent. The inference from these conclusions is that, for the higher molar mass examples of POE, a helical structure of the form proposed by Kjellander and Florin, with hydrocarbon groups in the interior of the helix, is a more likely result than that of Graham, which results in a considerable proportion of hydrocarbon surface being exposed to the solvent; however, the structure must accommodate three water molecules per ethylene oxide unit.

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REFERENCES

1   Tsuchida, E., Osada, Y. and Ohno, H. *J. Macromol. Sci.-Phys. B.* 1980, **17**, 683
2   Bekturov, E. and Bimendina, L. A. *Adv. Polym. Sci.* 1981, **41**, 99
3   Kabanov, V. A. and Papisov, I. M. *Polym. Sci. USSR* 1979, **21**, 261
4   Donners, W. A. B. *J. Polym. Sci.* 1987, **25**, 29
5   Malcolm, G. N. and Rowlinson, J. S. *Trans. Faraday Soc.* 1957, **53**, 921
6   Kagemoto, A., Murakami, S. and Fujishiro, R. *Makromol. Chemie* 1967, **105**, 154
7   Molyneux, P. 'Water, A Comprehensive Treatise' (Ed. F. Franks), Plenum Press, New York, 1975, Vol. 4, p. 569
8   Blandemer, M. J., Fox, M. F., Powell, E. and Stafford, J. W. *Makromol Chemie* 1969, **124**, 222
9   Maijgren, B. *Thesis*, Royal Institute of Technology, Stockholm, 1974
10   Kjellander, R. and Florin, E. *J. Chem. Soc. Faraday Trans. I* 1981, **77**, 2053
11   Liu, K.-J. and Parsons, J. L. *Macromolecules* 1969, **2**, 529
12   Koenig, J. L. and Angood, A. C. *J. Polym. Sci., Part A-2* 1970, **8**, 1787
13   Graham, N. B., Nwachuku, N. E. and Walsh, D. J. *Polymer* 1982, **23**, 1345
14   Graham, N. B., Zulfiquar, M., Nwachuku, N. E. and Rashidi, A. *Polymer* 1989, **30**, 528
15   Graham, N. B. and Zulfiqar, M. *Polymer* 1989, **30**, 2130
16   Graham, N. B., Zulfiqar, M., Nwachuku, N. E. and Rashid, A. *Polymer* 1989, **31**, 909
17   Char, K., Frank, C. W., Gast, A. P. and Tana, W. T. *Macromolecules* 1987, **20**, 1823
18   Polik, W. F. and Burchard, W. *Macromolecules* 1983, **16**, 978
19   Brown, W. *Macromolecules* 1984, **17**, 66
20   Michalczyk, A. and Burchard, W. *Eur. Polym. J.* 1989, **25**, 957
21   Franks, F. *Chem. Ind.* 1961, 204
22   Franks, F. and Eagland, D. *Crit. Rev. Biochem.* 1975, **3**, 165
23   Eagland, D. 'Water Science Reviews' (Ed. F. Franks), Cambridge University Press, **40**, 1989
24   Garvey, M. and Robb, I. D. *J. Chem. Soc. Faraday Trans I* 1979, **75**, 993
25   McMillan, W. and Mayer, J. *J. Chem. Phys.* 1945, **13**, 176
26   Franks, F., Pedley, M. and Reid, D. S. *J. Chem. Soc. Faraday Trans. I* 1975, **71**, 359
27   Barone, K., Castronuovo, G., Del Vecchio, P. and Elia, V. *J. Chem. Soc. Faraday Trans. I* 1988, **84**, 1919