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Temperature dependence of the virial coefficients and the chi parameter in semi-dilute solutions of PEG

This paper is dedicated to Prof. W. Ruland on the occation of his 80th birthday

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Abstract Poly(ethylene glycol) (PEG) with a molecular weight of about 4600 in semidilute solutions with D2O as solvent has been studied by small-angle x-ray scattering in a broad temperature range from 10 to 100° C at concentrations from 1wt% to 20wt%. The scattering from the PEG solutions can be very well described by a random phase approximation (RPA) type expression. The forward scattering of the chains is analysed by two different approaches: In terms of temperature dependent virial coefficients and in terms of the recently derived Flory-Huggins theory for polymers solutions with a temperature dependent chi parameter. The virial approach gives a theta temperature of 100° C. A satisfactory fit by the virial approach requires only a second and a forth order virial coefficient. In the Flory-Huggins theory a correction for the finite polymer volume fractions results in a lower value of the theta temperature of 86° C. The chi parameter varies from 0.32 at 10° C from 0.52 at 100° C. The analysis of the temperature dependence of chi shows that it is predominately due to entropic effects.

Introduction

Poly(ethylene glycol) (PEG) is probably the simplest water soluble synthetic polymer. Due to its biocompatibility it is used in a very broad range of pharmaceutical [1] and cosmetic products [2]. For example, amphiphilic block copolymers with one of the blocks being PEG are frequent components in pharmaceutical formulations and in drug delivery systems. It is the biocompatibility of the PEG corona of nano-sized drug delivery particles, which provides the ‘stealth’ properties, so that the particles are not immediately degraded by the immune system [3]

The PEG-water system is also an interesting system from a fundamental point of view due to the large change in solvent quality of water for PEG with variation of temperature. Water becomes a poorer solvent as the temperature is raised and it has a theta temperature of about 100°C.[4,5] The pronounced temperature dependence of PEG in aqueous solutions is crucial for the thermal stability of products containing the polymer. As an example of the influence of the temperature dependence of the solvent quality of water for PEG, one can mention the change in micelle structure and rheological properties of block copolymer micelles of PEG and poly(propylene oxide) at high temperature [6]

The change in solvent quality is associated with water molecules, which forms strong hydrogen bonds with the oxygen in the backbone of the PEG at low temperature.[7, 8, 9] As the temperature is increased, the hydrating water gradually disorders and the solvent quality gradually decreases. The change in the hydrating water is reflected in a large change in the apparent partial specific volume of the PEG chains.[10] The solvent quality is also directly reflected in the chain-chain interactions in dilute and semi-dilute polymer solutions. The present work is a study by small-angle scattering of such solutions of PEG in water in a broad temperature and concentration range.

Scattering techniques are well suited for investigating the structure and interactions in polymer solutions.

However, the interpretation of the scattering data depends crucially on whether suitable expressions are available for fitting the data. It has been demonstrated that the scattering intensity of semi-dilute solutions can be well described by a random phase approximation (RPA) expression, [11, 12] which in fact is also in agreement with suggestions by Zimm [13] and Benoit and Benmouna [14]. In the present work we have performed a small-angle x-ray scattering study (SAXS) of PEG in water. We apply the RPA expression to obtain information on the concentration effects and thus on the chain-chain interactions in the solutions as a function of temperature. The results are described by two different approaches: (i) In terms of temperature-dependent virial coefficients and (ii) in terms of a temperature-dependent Flory-Huggins chi parameter via recently derived expressions.

Experimental

The PEG homopolymer used in the study is PEG 4600 from Sigma-Aldrich. The polymer weight average molar mass was determined to be 4600 by MALDI-TOF mass spectroscopy and HPLC at the Danish Polymer Centre at Risø National Laboratory. A polydispersity index of 1.2 was calculated from the mass distribution. The polymer was used as received.

The samples were prepared by weight by dissolving PEG 4600 in D_2O (D purity higher than 99.9%) from Sigma-Aldrich. Samples with concentrations of 1, 2, 5, 10 and 20 wt% were mixed. The samples were left overnight and clear homogeneous solutions formed. D_2O was used in case future small-angle neutron scattering (SANS) would be performed, as the D_2O gives good contrast and low background in SANS.

SAXS measurements were performed on the pin-hole SAXS instrument at the University of Aarhus.[15] The instrument is a modified version of the original small-angle x-ray equipment known as the 'NanoSTAR', which was produced by Anton Paar, Graz, and distributed by Bruker AXS. The camera employs a rotating anode (MacScience with Cu anode, 0.3× 0.3 mm^2 projected source point, operated at 4.05 kW) and it has a three-pin-hole collimation. The instrument is optimised for solution scattering to have a high flux and a low background. The divergent Cu Kα radiation from the anode is monochromatized and made parallel by two cross-coupled Göbel mirrors. The samples are kept in a reusable home-built capillary holder with a quartz capillary with a pathlength of about 1.75 mm. The capillary is placed in the integrated vacuum chamber of the camera, and extra windows are avoided. The capillary holder is thermostated with a Peltier element which is computer controlled (Bruker AXS and Anton Paar). The temperature inside the capillary was checked by a thermoelement placed in the water-filled holder in vacuum. The temperature was varied from 10 to 100°C in steps of 10° C.

The sample detector distance is 66 cm and the beamstop is 3.0 mm in diameter. The instrument configuration gives access to a range of scattering vectors q from about 0.01 to 0.34 Å^{-1}, where the scattering vector modulus is given by $q = (4\pi/\lambda)\sin\theta$, where 2θ is the scattering angle and λ is the wavelength. The two-dimensional data sets are recorded using a two-dimensional position-sensitive gas detector (HiSTAR). The data were normalized to the integrated incident flux and sample transmission. The latter was measured indirectly by recording the integrated scattering from a strongly scattering sample (glassy carbon) with and without the sample inserted in the beam path before the glassy carbon. The spectra of all samples, corrected for variations in detector efficiency, were isotropic and the data were azimuthally averaged and corrected for spatial distortions. A pure D_2O samples was measured at the same temperatures as the samples and used for background subtractions. Finally the resulting data were converted to absolute scale using the scattering from pure water as a primary standard [16].

The apparent partial specific volume of PEG 4600 was determined from density measurements performed at 5–90°C with a DMA5000 densitymeter (Anton Paar) on solutions of PEG 4600 with concentrations 1, 2, and 5 wt%. The excess scattering length density of PEG in D2O was calculated from the partial specific densities.

Theory

For dilute solutions the scattering intensity can be described by the RPA/Zimm scattering cross-section expression [11,12,13,14]:

$$\frac{d\sigma(q)}{d\Omega} = cM_w\Delta\rho_m^2\frac{P(q)}{1+vP(q)} \tag{1}$$

where c is the concentration in g/mL, M_w is the weight-average molecular mass, and $\Delta\rho_m$ is the excess scattering length per unit mass of polymer. $P(q)$ is the single chain form factor and v is a parameter depending on the reduced concentration c/c^* and the binary cluster integral β, which describes the effective monomer-monomer interaction:

$$\beta = 4\pi\int r^2dr[1-\exp(-V(r)/kT)] \tag{2}$$

where k is Boltzmann's constant, T is the absolute temperature and $V(r)$ is the effective monomer-monomer interaction potential. For low concentrations (i.e. below the overlap concentration of the chains) v is proportional to the second virial coefficient A_2. At the theta temperature T_θ, the second virial coefficient A_2 vanishes and there are no concentration effects at low concentrations.

In the recently developed Flory-Huggins theory[12] for semi-dilute solution, (1) is still valid. A simple calculation shows that

$$v = \eta\frac{V_{PEG}}{V_{H2O}}\left[\frac{1}{1-\eta} - 2\chi\right] \tag{3}$$

where η is the polymer volume fraction, V_{PEG} is the PEG molecular volume, V_{H2O} is the volume of a water molecule, and χ is the temperature dependent Flory-Huggins interaction parameter. For $T \to T_\theta$ and small concentrations ($\eta << 1$), $\chi \to ½$ and $v \to 0$, so that the concentration effects also vanish for this expression, in agreement with behaviour of the Zimm expression at the theta temperature.

Considering higher order-terms in a virial expansion at $q = 0$ in terms of η, one has

$$v = \eta 2A_2M + \eta^2 3A_3M + \eta^3 4A_4M + \cdots \tag{4}$$

Equation (3) from the Flory-Huggins theory also contains higher-order terms. A series expansion gives:

$$v = \eta\frac{V_{PEG}}{V_{H2O}}\left[1-\eta-\eta^2-\eta^3-\eta^4\cdots-2\chi\right] \tag{5}$$

so that:

$$2A_2M = \frac{V_{PEG}}{V_{H_2O}}[1-2\chi], \quad 3A_3M = -\frac{V_{PEG}}{V_{H_2O}},$$
$$4A_4M = -\frac{V_{PEG}}{V_{H_2O}}\cdots \tag{6}$$

which provides a direct link between χ and A_2, and which in addition shows that all higher virial coefficient are constant in the Flory-Huggins theory. Therefore the concentration effects do not vanish at the theta temperature at finite concentrations.

In the model we used the form factor of semi-flexible chains [17]. The data at low concentration and at high temperature, where the concentrations effects are very small, were fitted with the form factor without inclusion of concentration effects. This gave a radius of gyration of R_g = 26 Å, which was kept fixed while fitting the RPA expression (1) to all the data.

At good solvent condition where the chains have self-avoiding configurations, an increase in concentration leads to a screening of excluded volume effects as predicted by Flory. However, this effect is not directly observable in the recorded data since it occurs at low q where nominator and denominator in the RPA expression display similar q dependence so that the intensity is constant in this region. In addition the excluded volume effects are expected to be small since the chains are relatively short, i.e. L/b = 45 [18,19]. Therefore the effects of screening of excluded volume interactions were not included in the form factor.

The expression (1) was fitted to the data and the effective forward scattering of the chains

$$P'(0) = \frac{1}{1+v} \tag{7}$$

was used as a fit parameter.

Results

The SAXS data are shown in Fig. 1 at three different temperatures. The data have been normalized by the concentration and by the contrast factor $\Delta\rho^2$ as calculated from the partial specific volumes. The latter was done in order to eliminate the effects of temperature dependence of this prefactor. An example of the influence of this normalization is shown in reference [10]. At low q, the data from some of the samples show an upturn at low q. This is due to the formation of a small fraction of larger clusters and it has recently been shown that it has its origin in chain end effects.[20] Note that this contribution is absent at the highest temperature. The data clearly shows that the concentration effects become weaker at elevated temperatures. At 100 °C only the 10 wt% and 20 wt% data clearly deviates from the other samples.

Figure 2 displays the data for selected temperatures for the 1, 2, 5, and 10 wt% samples. The temperature dependence is weak for the 1 wt% sample. The effects become increasingly more important as the concentration is increased.

Figures 1 and 2 also contain the fits by the RPA expression. The fits are satisfactory except at low q for the samples with a significant cluster contribution. In addition the fit to the 20 wt% data deviate significantly from the data at low q.

Virial analysis

The results for $P'(0)$ from the fits are shown in Fig. 3. There is a clear increase in $P'(0)$ with temperature at all concentrations, which is in agreement with the weakening of the polymer interactions with increasing temperature. In a first step of an analysis of $P'(0)$, we will use only the second virial coefficient and assume the simplest functionality. We set $v = 2McA_2$, where M = 4600 and take c as the weight fraction of the solution. Furthermore, we use the proportionality $A_2 = \mathrm{A}_2^{\mathrm{fit}}\,(T - T_\theta)$ and fit the $P'(0)$ data as a function of T. This provides a first crude estimate of the value of T_θ (and A_2^{fit}). The fits are shown in Fig. 3 and the corresponding values for T_θ are, respectively, 94+/−6, 97+/−2, 100+/−1, 105+/−2, and 109+/−3°C, for 1, 2, 5, 10 and 20 wt%. For the three lowest concentrations, the values are in excellent agreement with the expected value of about 100° C[5]′. At higher concentrations, the higher virial coefficients are important and these do not vanish at the theta temperature. We have furthermore, for, respectively, 1, 2, 5, 10 and 20 wt%, A_2^{fit} = 0.000056+/−0.000008, 0.000058+/−0.000003, 0.000065+/−0.000003, 0.000074+/−0.000004, and 0.000135+/−0.000014 (g/mol °C)$^{-1}$. The increase of the value at the highest concentration also shows the influence of higher order virial terms at high concentration.

As the data for $c \leq 5\%$ are not influenced by higher order virial terms, one can perform a simultaneous fit of these data with the same value for T_θ (fit not shown). One obtains by this for A_2^{fit} = 0.000057+/−0.000002 (°C)$^{-1}$ and T_θ = 100.1+/−1°C, where the theta temperature is again in excellent agreement with the expected value.

At high concentrations (10 and 20 wt%), the contributions from the higher order virial coefficients leads to systematic errors and higher order terms have to be included in order to obtain good fits to the data. Fitting each temperature individually shows that the A_3 term is so small that it can be neglected, whereas the A_4 term is significant. The temperature dependence of it can be reproduced by an expression with a term which vanish at T_θ and a residual term: $A_4 = \mathrm{A}_4^{\mathrm{fit}}\,(T - T_\theta)^3 + \mathrm{A}_4^{0}$. In this expression A_4^{fit} and A_4^{0} are additional fitting parameters. The equation (5) with this expression and the corresponding one for the second order virial coefficient gives an excellent simultaneous fit to all the data (Fig. 3(b)). The results from this fit are A_4^{0} = 99.5+/−0.5°C, A_2^{fit} = 0.000057+/−0.00001 1/°C, A_4^{fit} = (1.97+/−0.09)×10^{-7} (g/mol)$^{-1}$(°C)$^{-3}$, and A_4^{0} = 0.0215+/−0.0009 (g/mol)$^{-1}$.

▶

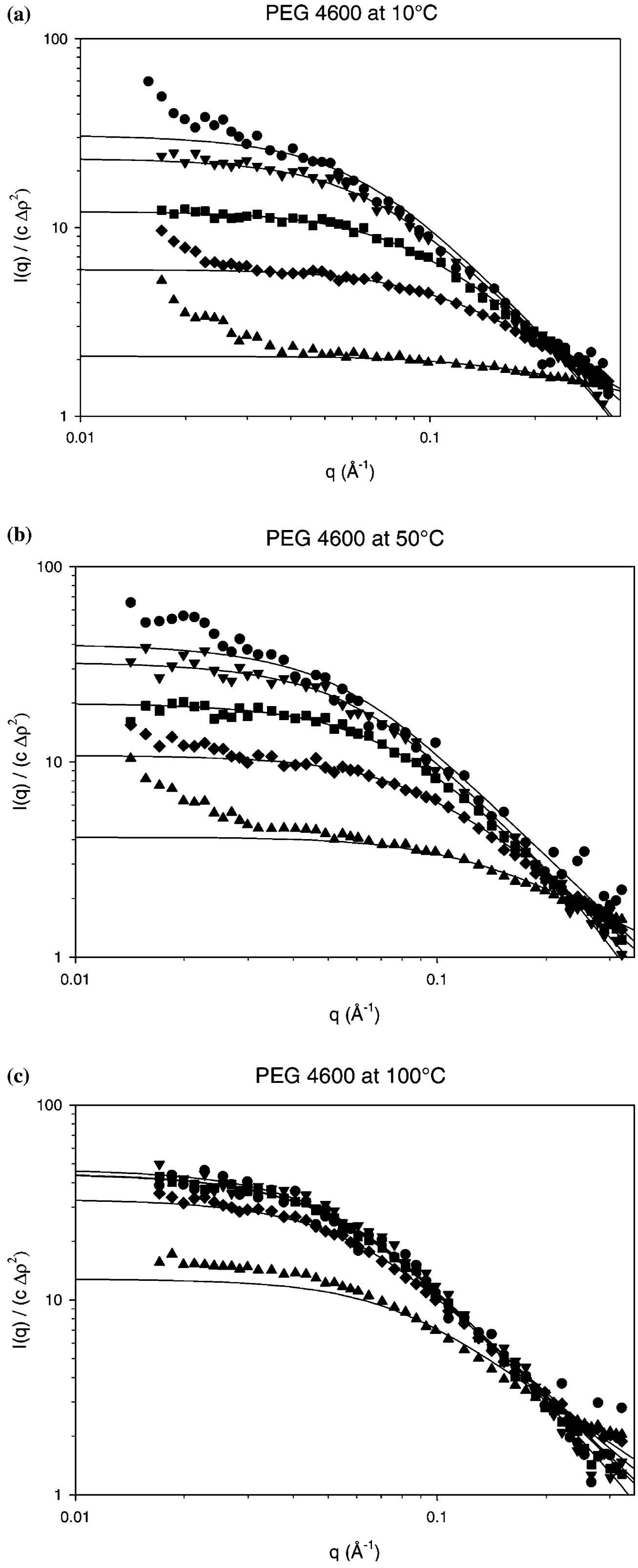


Fig. 1 SAXS data with fits (curves) for PEG 4600 solutions at fixed temperature as a function of concentration. (a) 10°C (b) 50° C (c) 100° C. Signatures: 1 wt% circles, 2 wt% triangle down, 5 wt% square, 10 wt% diamond, 20 wt% triangle up. The data have been divided by the square of the excess electron density ($\Delta\rho$ was in units of e/Å^3) of the PEG chains in order to eliminate the influence in the plot of the change in contrast with temperature

Flory-Huggins Theory

As already mentioned, the higher order terms are already included in the Flory-Huggins theory and all temperature dependence is assigned to the chi parameter (3). In a first approach we used a chi parameter at each temperature to fit the data. The polymer volume fraction η, the PEG volume V_{PEG}, and the volume of a water molecule V_{H2O} were calculated at each temperature from the density results. Since the osmotic pressure is related to the number-averaged molecular mass, V_{PEG} was taken as number average volume. The expression did not fit the high volume fraction data at high temperature, and therefore only the data for $c \leq 5$ wt% were fitted and the curves for c > 5 wt% calculated from the resulting fit. The curves are shown in Fig. 4(a), where linear interpolations between the values at the data points have been introduced. One sees that the model reproduces the concentrations effects very well at low temperature even at the highest concentration, however, at high temperatures, where the system approaches the theta condition, the model overestimates the concentration effects. The chi parameter corresponding to the fit is shown in Fig. 5. It is around 0.32 at 10°C and goes smoothly to the theta value of 0.5 between 80 and 90°C. For comparison, for polystyrene in toluene, for which the solvent is considered to be a good solvent, the chi parameter is about 0.44,[21, 22] so the solvent conditions are indeed very good for PEG in water at low temperature. The volume fraction correction in (3) to the theta condition $\chi = ½$ leads to a lowering of the theta temperature compared to the value found in the virial analysis.

In the final step of the analysis, we assumed a temperature dependence of χ:

$$\chi = 0.5 + \chi_1(T - T_\theta) + \chi_2(T - T_\theta)^2 \tag{8}$$

where the second term is included due to the curvature of temperature dependence of χ as observed in the previous fit (Fig. 5(a)). The number of fit parameters is in this way greatly reduced since we do not need a chi parameter at each temperature. Again only the data for $c \leq 5$ wt% were fitted and the curves for c > 5 wt% calculated from the resulting fit (Fig. 4(b)). Also for this fit, the model overestimates the concentration effects at high temperatures, where the system approaches the theta condition. The chi parameter is shown in Fig. 5(a) and agrees very well with the values determined by having individual fit parameters for each temperature. The

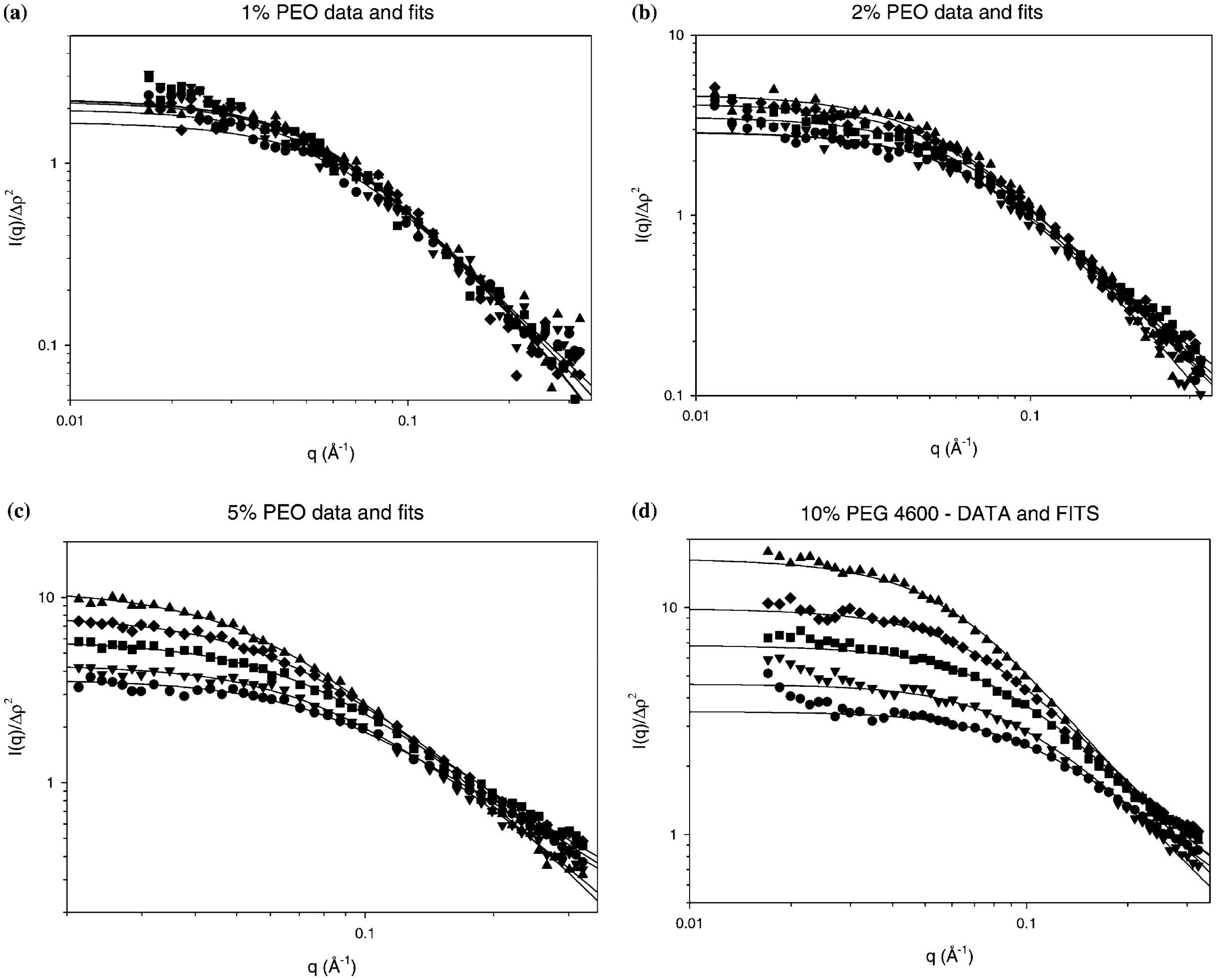


Fig. 2 SAXS data with fits (curves) for PEG 4600 solutions at fixed concentration as a function of temperature. (a) 1 wt% (b) 2 wt% (c) 5 wt% (d) 10 wt%. Signatures: 20°C circles, 40°C triangles down, 60°C squares, 80°C diamonds and 100°C triangles. The data have been divided by the square of the excess electron density of the PEG chains in order to eliminate the influence in the plot of the change in contrast with temperature

values for the two coefficients in the expression for chi are $\chi_1 = 0.00142+/-0.00009$ and $\chi_2 = -0.000011+/-0.000002$, and the theta temperature is 85.7 +/−1.1°C

In a previous light scattering study, Venohr et al. [23] used the expression

$$\chi = \alpha + \frac{\beta}{T} \tag{9}$$

to describe the temperature dependence of χ. In order to investigate whether the χ follows this relation, we have in Fig. 5(b) plotted the χ versus $1/T$ using the values obtained by fitting the individual temperatures. The data shows a remarkable linear behaviour and we have therefore used the expression (9) for chi and fitted the forward scattering $P'(0)$. We have also in this case only fitted the data for $c \leq 5$ wt% and calculated the curves for c > 5 wt% due to the overestimation of the concentration effects close to the theta temperature. The agreement for this two-parameter fit is as good as for the three-parameter fit using (8). The results are $\alpha = 1.156+/-0.002$ and $\beta = -235.3+/-0.9$ K.

In the Flory-Huggins theory [24]

$$\chi = \frac{z\Delta\varepsilon}{kT} = \frac{z\left(\varepsilon_{pw} - \frac{1}{2}\left[\varepsilon_{ww} + \varepsilon_{pp}\right]\right)}{kT} \tag{10}$$

where z is the coordination number on the lattice, k is Boltzmann's constant and $\Delta\varepsilon$ is the free energy of forming a polymer-water contact. In the last expression ε_{pw} is the free energy of a polymer-water contact, ε_{ww} is the free energy of a water-water contact, and ε_{pp} is the free energy of a polymer-polymer contact. $\Delta\varepsilon$ can also be expressed in terms of an enthalpic and an entropic contribution $\Delta\varepsilon = \Delta H - T\Delta S$. So in agreement with reference (4), the two terms in (9) can be identified with, respectively, an entrophy and an enthalpic energy term:

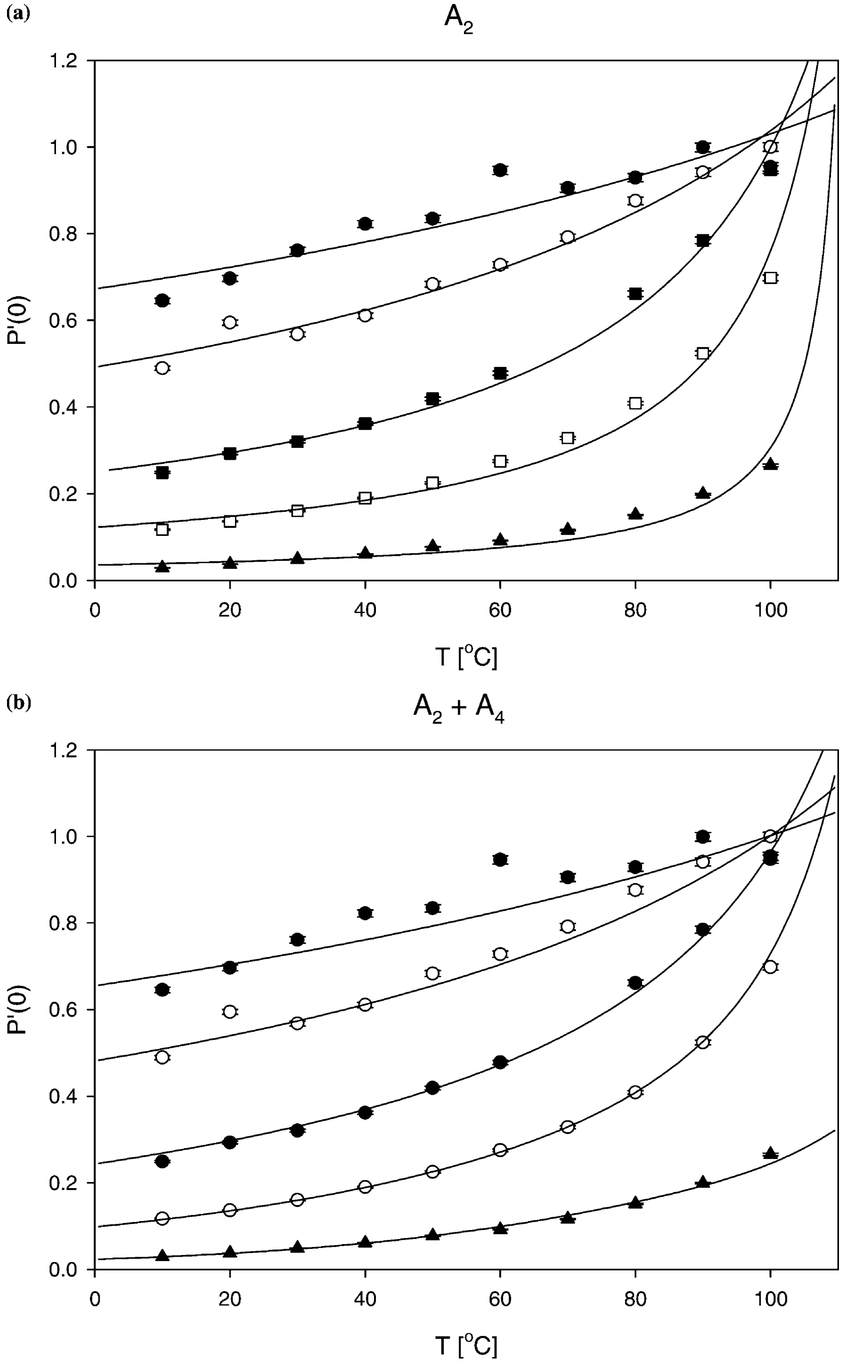


Fig. 3 The forward value of the effective single chain form factor of the PEG chains at 1%wt (filled circles), 2 wt% (open circles), 5 wt% (filled squares), 10 wt% (open squares) and 20 wt% (filled triangles). The curves are fits with virial expressions. (a) Including only a second virial coefficient, which goes linearly to zero at the theta temperature. (b) Including both a second and a fourth virial coefficient with temperature dependence (see text for details)

$$\chi = \chi_{\Delta S} + \frac{\chi_{\Delta H}}{T} \tag{11}$$

If it is assumed that ΔH and ΔS are independent of temperature, a temperature change from 10 to 100°C as in the present work, corresponds to ratios of $\Delta H/\Delta\varepsilon$ and $\Delta S/\Delta\varepsilon$ of

$$\Delta H/\Delta\varepsilon = 0.31 \text{ and } \Delta S/\Delta\varepsilon = 0.69 \tag{12}$$

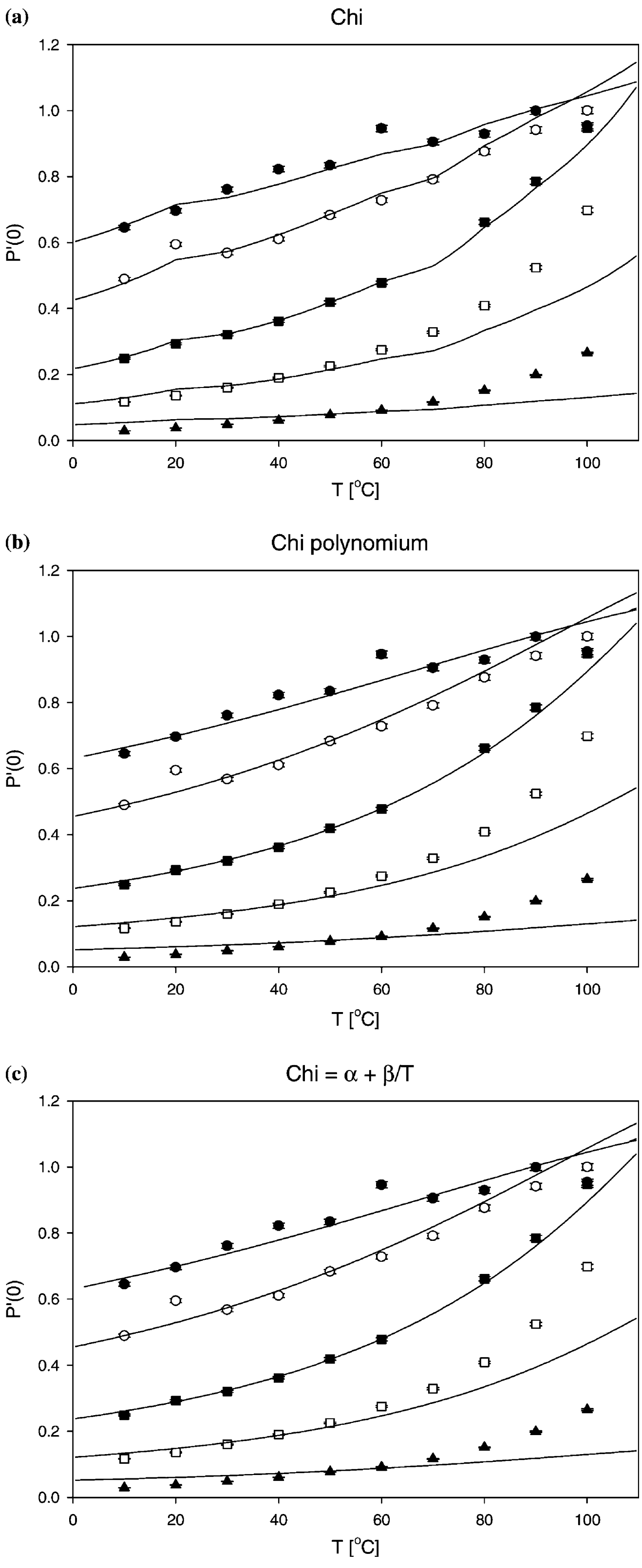
and one sees that the free energy change is dominated by entropy.

Discussion

Scattering studies of polymer solutions can be performed using light [22], neutrons [25] or x-rays. The former is the

▶

Fig. 4 The forward value of the effective single chain form factor of the PEG chains with signatures as in Fig. 3. The curves are fits using the Flory-Huggins theory. (a) With individual chi parameters at each temperatures and interpolations. (b) A second order polynomium for chi. (c) Using $\chi = \alpha + \beta/T$



choice for high molecular weight polymers, whereas the two latter are the choice for lower molecular weights. For the PEG-water system the scattering contrast is favourable for light and for neutrons (when using D_2O as solvent), whereas it is weak for x-rays. In spite of this, the present study employs small-angle x-ray scattering on a laboratory-based instrument. Such a study of a weakly scattering system has become feasible due to the developments in optimised instrumentation for solution scattering[15].

In the present study experiments have been performed as a function of concentration in a particularly broad temperature range. Very pronounced concentration and temperature dependence have been observed. The forward scattering was derived from applying the RPA expression to the SAXS data. The data could be fitted with a temperature- and concentration independent radius of gyration for the chains.

Analysis of the forward scattering for low concentrations in terms of a virial expansion gave $A_2 \approx 0.005$ (g/ mol)$^{-1}$ at 10°C in agreement with results by Venohr et al. for PEG with a molecular weight of 10000. The linear temperature dependence and the theta temperature of 100°C are also very similar to that found Venohr et al. Analysis of our data for higher concentrations showed that the data could be fitted perfectly with only a second and a fourth virial coefficient, which both depend on the temperature separation from the theta point. The second virial coefficient depends linearly on this temperature separation whereas the fourth virial coefficient depends on the separation to the power three and in addition has a residual value at the theta point. Due to the similarities of the temperature dependence of the two virial effects we suggest that the temperature dependent part of both coefficients is related to the effective pair potential and that the residual of the fourth coefficient at the theta point originates from steric contributions which are not vanishing at the theta point.

The application of the Flory-Huggins theory to the data showed that this theory gives a good description of the data except close to the theta temperature where it exaggerates the concentration dependence of the forward scattering. The magnitude and the temperature dependence of the chi parameter is in good agreement with previous findings [4,23] The temperature dependence of chi follows $\chi = \alpha + \beta/T$ and when making the connection to the interaction energies in the Flory-Huggins theory one can identify α with an entropic free energy contribution and β with an enthalpic. Using the

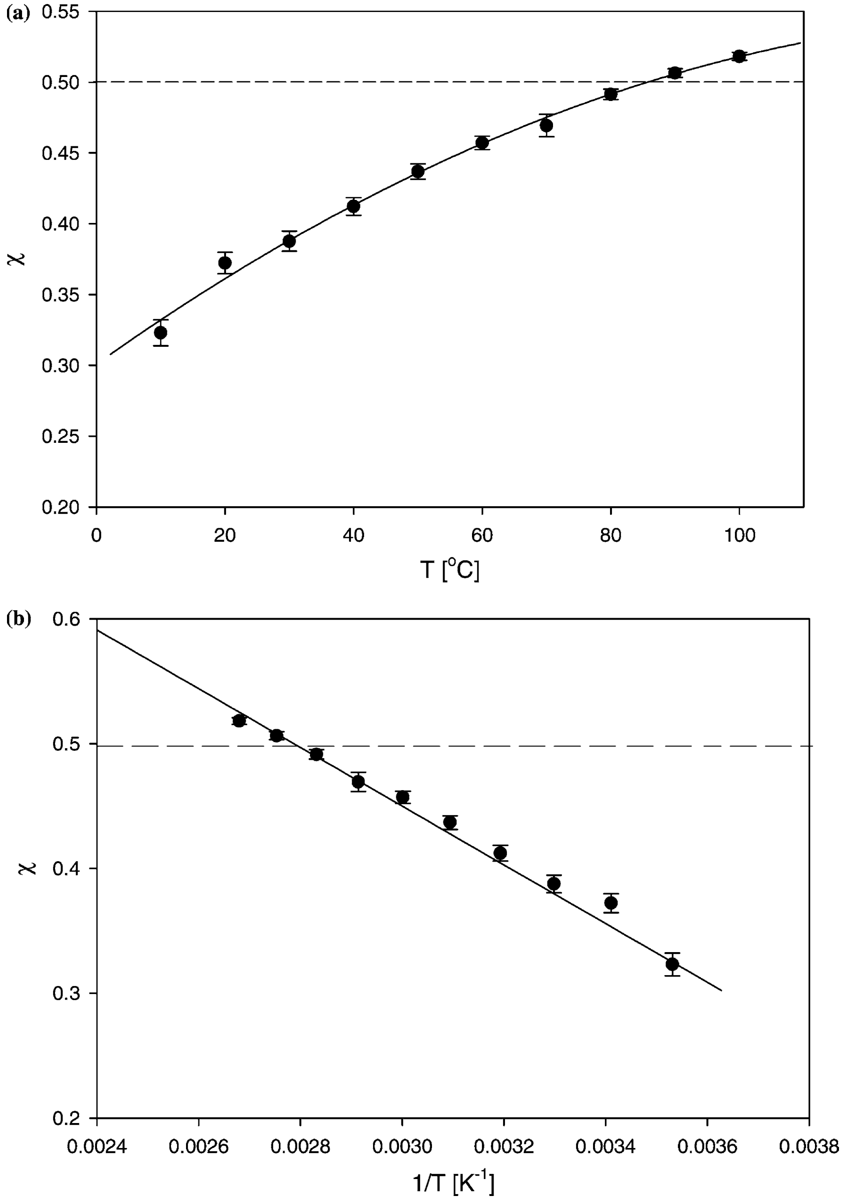


Fig. 5 The temperature dependence of the chi parameter. The points are the individual chi parameters at each temperatures. (a) The curve is from a second order polynomium for chi. (b) The curve is $\chi = \alpha + \beta/T$ from the fit in 4(c)

observed temperature dependence of chi, one finds that about 70% of the change in the free energy is entropy related and 30% are enthalpy related. This is en good accordance with the suggestion [8,9] that the change in solvent quality is due to a gradual disordering of water molecules which are tightly bound to the PEG chain and relatively well-ordered. This conclusion is further cooperated by the large change in apparent partial specific volume of PEG in water [10]. As the temperature is increased the PEG chains have a gradual increase in the apparent volume due to the disordering of the tightly bound water.

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