

Apparent Specific Volume Measurements of Poly(ethylene oxide), Poly(butylene oxide), Poly(propylene oxide), and Octadecyl Chains in the Micellar State as a Function of Temperature

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Apparent specific densities of aqueous solutions of the diblock copolymers $C_{18}(EO)_{100}$, $C_{18}(EO)_{20}$, and $(EO)_{92}(BO)_{18}$ and the triblock copolymers $(EO)_{25}(PO)_{40}(EO)_{25}$ and $(EO)_{21}(PO)_{47}(EO)_{21}$ in the micellar state have been measured over a temperature range from 10 to 90 °C at concentrations between 1% and 5%, using an oscillating tube densitometer. From these measurements, apparent specific volumes of poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), poly(butylene oxide) (PBO), and octadecane in the micellar state have been determined. The composition of the block copolymers was checked by NMR spectroscopy. Results were compared with published data for the polymers and bulk values for octadecane, respectively. The apparent specific density of PEO chains in the dissolved state was also measured for PEG4600 solutions at different concentrations and compared with results in the micellar state. The results presented in the paper are crucial in connection with analysis and modeling of small-angle X-ray scattering (SAXS) data from polymer and block copolymer micellar systems. PEO and PPO have a relatively low apparent partial specific volume in water at low temperatures. It is associated with water molecules making strong hydrogen bonds with the oxygen atoms on the polymer backbone. These water molecules gradually become disordered when the temperature is increased and the polymer apparent specific volume increases. For PBO in the micellar cores of PBO-PEO block copolymer micelles and in PNIPAM microgels, pronounced temperature dependence with the same origin is also found. The application of the derived results for the apparent specific volume of PEO for deriving contrast factors is demonstrated and the results are used in the analysis of SAXS data for semidilute solutions of PEG4600 in a broad temperature range.

Introduction

Block copolymers containing poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), and poly(butylene oxide) (PBO) blocks are the subject of intense interest (see ref 1 and references therein). In many results arising from fundamental studies and industrial development, the specific volume as a function of temperature is an essential property. However, only very limited reliable data can be found in the literature. We have a particular interest in the precise knowledge of the apparent specific volume of each block in a block copolymer solution, as this information is necessary for the analysis and modeling of small-angle X-ray scattering (SAXS) data² where the electron density of the components determines the contrast of these. We use the term *apparent* as we in our analysis associate all changes in specific density with the dissolved molecules, although the solvent in the vicinity of the dissolved molecules in most cases changes its density. The scattering length density of any substance in solution is directly related to the density of the substance (and of the solvent) and therefore precise values of the apparent specific density of the components as a function of temperature are required. The contrast factor for SAXS is given by the

difference in electron density of the dissolved molecules and the solvent. As electron densities of organic molecules are quite similar in magnitude to those of the solvent, small errors in specific volumes can lead to very large changes in the contrast factors. For small-angle neutron scattering (SANS) it is in most cases less important to have accurate values for the specific densities. Most protonated molecules are measured in deuterated solvents to enhance the contrast, and as the scattering length density of protonated and deuterated organic substances is very different, the contrast factor is less sensitive to the values of the specific densities.

In aqueous solution, block copolymers behave like surfactant molecules and build a wide variety of aggregates as a consequence of their amphiphilic character.³ Micelles with a spherical shape are typical; the hydrophobic block is gathered into a spherical core and the hydrophilic blocks are solvated by water. In such a solution, the conditions encountered by the blocks are quite different from the case of a pure polymer dissolved in a solvent. In the same way, the effect of temperature on the apparent specific volume of the two components of a diblock copolymer in a solvent will depend on the change of solvent quality for each block with temperature. More generally, it is known that micelles can undergo structural rearrangements at different temperatures depending on the composition, the length of the blocks, and the presence of other species in solution.

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These transitions are particular to each of the investigated surfactant and block copolymer systems.

The physicochemical and thermodynamical properties of block copolymers and their mixture have been extensively studied, both in the melt and solid state, as well as dissolved in different kinds of solvents. Due to the large interest in the scientific community and major applications in textiles, in cosmetics, as antifoaming agents, as chemical intermediates, etc., PEO/PEG systems have attracted a lot of attention, and a large number of papers have been dedicated to these systems, in particular the determination of critical point data,⁴ θ temperature,^{5–7} the study of the interactions with the solvent,⁸ and other related properties.^{9,10} Values of the specific volume have been reported, but we find considerable disagreement between the available data, partly because of the different conditions of investigation. In addition, most of the studies are limited to a smaller temperature range than the one investigated in the present work, or to polymers with very different molar masses.

The effect of chain length is important because the properties of hydroxy-ended oligomers are strongly influenced by hydrogen-bonding interactions of the end groups. Therefore, the smaller the chain, the more pronounced are such effects. This can be avoided by converting the glycols into dimethyl ethers as done in a study of poly(butylene oxide)- and poly(ethylene oxide)-specific volumes in the melt state.¹¹ In this study, methylated forms of the polymers of different molar masses, but under 5000 g/mol, are used in the bulk state and specific volumes between 30 and 90 °C are determined with pycnometers. The authors find a considerable dependence on molecular weight of the polymers, which is used to extrapolate values to infinite chain length. However, when compared with previous data for hydroxy-ended poly(butylene oxide), the dependence of methyl-ended poly(butylene oxide) on chain length is shown to be much more pronounced. The authors argue that in the case of hydroxy-ended polymers, the increase in free volume caused by the end group is compensated by an increase in cohesion due to hydrogen bonding, so that the properties of short hydroxy-ended polymers is in fact close to their high molar mass analogues. This is confirmed by studies of excess volumes of poly(ethylene glycol) in water,^{12,13} where PEG of different masses are used at a given temperature. It is shown that the specific volume varies only very little with the molar mass, neither in the melt state nor in aqueous solution. The authors of both studies find negative values of the excess volume in water that become more negative at decreasing temperature and increasing molecular weight, which they relate to favorable interactions between PEO molecules and water due to the formation of hydrogen bonds. Poly(propylene oxide) aqueous solutions of molar mass 400 (PPO 400) have been the subject of a rheological and densitometric study,¹⁴ which led to similar conclusions.

Other especially relevant studies concern systems where the copolymer is in the micellar state, which is also the one considered in our study. Wen et al.¹⁵ investigated different kinds of Pluronics (PEO–PPO–PEO) with different compositions and reported data on the effect of temperature, relative molar mass, and hydrophilic/hydrophobic (PEO/PPO) mass ratio of the copolymers on the apparent specific volume and other thermodynamic properties of aqueous solutions of a number of these copolymers. We use some of their results here for comparison. Another related study has been published by Armstrong and al.,¹⁶ where differential scanning densitometry is used to investigate the phase transition properties of a series of Pluronics in water. From their results for the apparent partial specific volume as a function of temperature, we derive values of the

specific volume of PEO and PPO by making the assumption that the block's contributions are additive and we compare the data with our own results.

The results for the block copolymer can also be compared to those for short-chain surfactants. In a study¹⁷ of $C_{12}(EO)_j$ micellar solutions with j between 5 and 8, the authors find apparent densities for the liquid surfactants, which correspond to a linear combination of the two components; however, with a systematic discrepancy that they attribute to the presence of an intermediate region, where the head and tail terminations are mixed together. This intermediate region at the hydrophobic/hydrophilic interface could also be present in micellar aggregates in water. However, they consider that for micellar solutions in water, the density of the hydrophobic region can be considered equal to that of the corresponding bulk oil. In the current study we check this assumption, by comparing bulk values from the literature¹⁸ with those determined for the C18 (octadecyl) chains in the Brij micelles using two different molecular weight Brij block copolymers.

In the present paper, we focus on the determination of the apparent specific volume of different copolymers in the micellar state over a wide temperature range, which fills a gap in the literature. The results are discussed in terms of hydrogen bonding and changes in solvation with varying temperature. It is furthermore demonstrated how the results can be applied in the analysis of SAXS data to account for changes with temperature which are only due to changes in contrast.

Experimental Section

Materials. $C_{18}(EO)_{100}$ block copolymer (Brij700) and $C_{18}(EO)_{20}$ (Brij78) were obtained from Sigma-Aldrich and used as received. The diblock copolymer $(EO)_{92}(BO)_{18}$ comes from the group of Colin Booth, University of Manchester, UK, and the triblock copolymers $(EO)_{25}(PO)_{40}(EO)_{25}$ (P85) and $(EO)_{21}(PO)_{47}(EO)_{21}$ (P94), commonly known as Pluronics, were obtained from BASF. The PEG4600 was from Sigma-Aldrich. H_2O Millipore was used as solvent. Solutions at weight fractions 1%, 2%, and 5% were prepared by dissolving appropriate amounts of polymer in H_2O . In a few of the measurements, D_2O from Sigma-Aldrich was used as solvent.

Densitometry. Solution densities were determined with a densitometer DMA 5000 (Anton Paar, Graz), which uses the oscillating-tube technique. The density determination is based on measuring the period of oscillation of a vibrating U-shaped hollow tube that is filled with the sample and using the relationship existing between the period of oscillation and the density. This relationship holds as long as the sample is not too viscous, otherwise the density has to be corrected to take into account the modified elastic modulus of the U tube.¹⁹ The densitometer was calibrated daily at 20 °C, using air and water as reference samples. The sample volume needed is approximately 1.5 mL and each measurement was repeated at least twice in the same day with fresh samples. The temperature was increased from 10 to 90 °C in steps of 5 deg with an accuracy of 0.002 °C. The measurements were run in the slow equilibrium mode (about 15 min equilibration) to ensure the highest possible quality of data. The accuracy of the data was estimated from the average deviation between the data sets. Evaporation of water in the empty space in the vials and higher probability of formation of small bubbles lead to an increasing error on the measured data at high temperatures. For pure water the accuracy of the density measurements is estimated as ± 0.000005 g/cm³ in the whole temperature range. For the other samples, the accuracy is ± 0.000020 g/cm³ from 10 to 50 °C and ± 0.000050

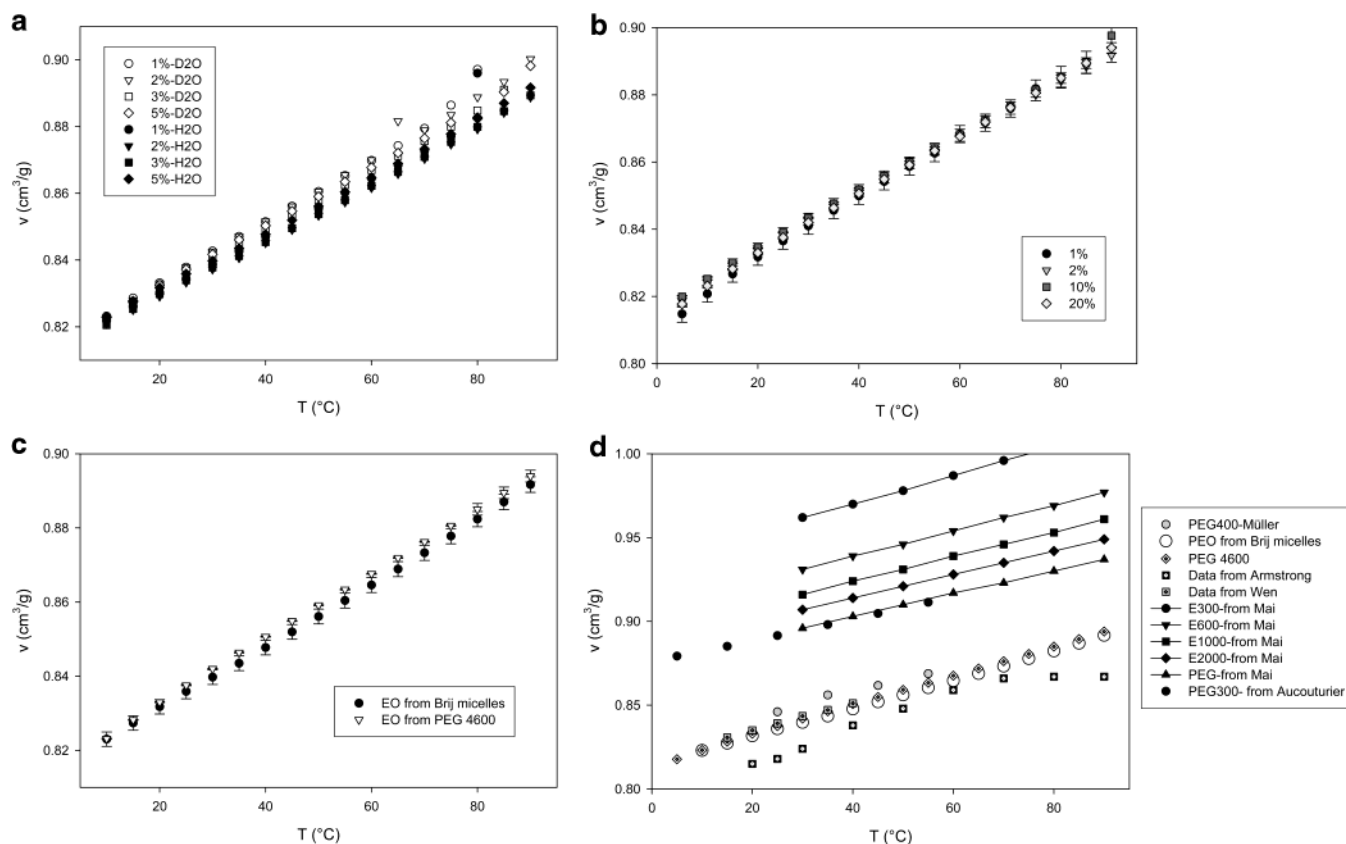


Figure 1. (a) Apparent specific volume of PEO from Brij micelles at different concentrations in H₂O and D₂O. (b) Apparent specific volume of PEO from PEG4600 solutions at different concentrations in H₂O. (c) Apparent specific volume of PEO from Brij micelles (5% in H₂O) and from the homopolymer (average values from different concentrations of PEG4600 in H₂O). (d) Apparent specific volume of PEO: comparison between previous literature data and results from this study.

g/cm³ from 60 to 90 °C. The errors on concentrations are estimated not to exceed a few %.

Methods. The two polymers Brij78 and Brij700 were used together to deduce the specific volumes of the PEO and C18 blocks in the micellar state, using 1%, 2%, 3%, and 5% polymer solutions in H₂O and D₂O. The specific volumes of PBO and PPO were then calculated by using the calculated specific volumes obtained for PEO with the help of results for respectively (EO)₉₂(BO)₁₈ and P85/P94 solutions at weight concentrations of 1% and 2%. The specific volume of PEO chains dissolved in water was deduced from 1%, 2%, 10%, and 20% PEG4600 solutions. The analysis of the data is done in the following way: The measured density in g/cm³ is converted to apparent specific volume of the solute by

$$v_{\text{solute}} = \left(\frac{1}{c_{\text{solute}}} \right) \left(\frac{1}{\rho_{\text{m}}} \right) - \left(\frac{1 - c_{\text{solute}}}{c_{\text{solute}}} \right) \left(\frac{1}{\rho_{\text{H}_2\text{O}}} \right) \quad (1)$$

where ρ_{m} is the measured density of the sample, $\rho_{\text{H}_2\text{O}}$ the measured density of water, and c_{solute} the weight fraction of the polymer. In the case of a copolymer consisting of two blocks, B1 and B2, assuming additivity of the volume contributions of B1 and B2, the apparent specific volume of the copolymer can be estimated as

$$V_{\text{polymer}} = m_{\text{B1}} v_{\text{B1}} + m_{\text{B2}} v_{\text{B2}} \quad (2)$$

where m_{B1} and m_{B2} are the mass fraction of the two blocks B1 and B2, and v_{B1} and v_{B2} are the specific volume (in cm³/g) of B1 and B2 in the polymer, respectively.

NMR Measurements. The nominal composition of the block copolymers was determined by ¹H NMR. The NMR experiments were carried out on a VARIAN UNITY 500 spectrometer. The polymers were dissolved in either CDCl₃ or D₂O. The relaxation delay (60 s) was chosen much longer than all the relevant relaxation times, which were 0.8–1.2 s as measured on P94 in CDCl₃ and Brij78 in H₂O, and 8–10 s for the HDO resonance of D₂O. Care was taken to position the signals to cause minimum distortion by the filter. The nominal composition was deduced from the integral of the proton signal of the repeat units and was independent of the solvent. Reproducibility of the experiments was better than 3%. For C₁₈(EO)₁₀₀, C₁₈(EO)₂₀, and (EO)₉₂(BO)₁₈, the experimental results lie very close to the nominal values within less than 2% error. However, for the triblock copolymers P85 and P94 with formula (EO)_{*e*/2}(PO)_{*p*}-(EO)_{*e*/2}, we find a significant discrepancy, i.e., a value of *e/p* equal respectively to 1.42 instead of 1.25 and 1.09 instead of 0.89. Surprisingly, it turned out that when the nominal values were used, the calculated densities for PPO were much closer to the values expected from previous literature values, and closer to each other by comparing values extracted from each of the Pluronics. We do not have at the moment any explanation for this result. We looked very carefully to the NMR spectra for broad components, which might have been missed, but we were unable to locate such components. For the results for the Pluronics presented in this paper, we have used the nominal compositions.

Results and Discussion

PEO. Figure 1a shows the temperature dependence of the apparent specific volume of poly(ethylene oxide) as determined

from measurements of micellar solutions of the block copolymers $C_{18}(EO)_{20}$ and $C_{18}(EO)_{100}$ at different concentrations in D_2O and H_2O . The curves show a regular increase with temperature throughout the temperature range studied, consistent with the usual thermal expansion. We do not expect any effect of concentration: a micellar concentration up to 5% should be sufficiently low to avoid any pronounced intermicellar interactions such as corona overlap, which could affect the specific volume of PEO. The results in Figure 1a show no systematic effect of concentration, and the small differences between the data sets are within the uncertainty range (the error bars are not shown in this plot for the sake of clarity). The reproducibility is usually better at higher concentration, as the relative contribution of the solute in the density values becomes more important. In the same way, the measurements in D_2O are more difficult than in H_2O as this solvent rapidly exchanges deuterium with hydrogen in atmospheric water. This effect can be significant when using a highly sensitive instrument such as the DMA 5000. However, the plot indicates a systematic isotope effect on the specific volume of ethylene oxide, which becomes more pronounced as the temperature increases. Since the mass of deuterium is larger than that of hydrogen, the hydrogen bonds are relatively stronger in D_2O than in H_2O at the same temperature. Higher values of the specific volume of PEO in heavy water can be related to the stronger hydrogen bonding between the water molecules of D_2O . This would lead to a relative reduced strength of interaction between the PEO and D_2O molecules, which would give a more disordered state of the water molecules in the neighborhood of the PEO chains in D_2O than in H_2O .

Figure 1b shows an analogue plot of the specific volume of PEO but obtained from a solution of PEG4600 (about 100 EO units) dissolved in water. A mass spectrometry analysis (MALDI-TOF) and size exclusion chromatography give a weight-average molecular weight of 4300 and a polydispersity index of 1.2. The typical chain size of this polymer is of the same magnitude as the PEO chains of Brij700. The data obtained at concentrations ranging from 1% to 20% show a good reproducibility and have small error bars. Such results are indeed obtained in a very straightforward way, as they are directly deduced from the measurements after subtracting the contribution of the solvent. It is interesting to observe that even at a concentration of 20% polymer, the behavior remains unchanged and no significant concentration effects show up. For micellar solutions of Brij such a concentration-independent behavior is also expected, since a low polymer concentration already corresponds to a high local concentration of the PEO chains, which concentrate in the corona of the micelles. In the case of PEG solutions, the good ability of water to dissolve PEO chains at room temperature makes the dissolution of large amounts possible. Previous measurements of the densities of PEG400 solutions at concentrations from 10% to 100% by Müller et al.¹³ show that it is only for concentrations higher than 50% that the specific volume of PEO starts to increase significantly.

Figure 1c shows a comparison of the apparent specific volume of PEO in the Brij micelles (obtained from a 5% solution in H_2O) and in the homopolymer solutions (average value from measurements at various concentrations). We note that the behavior as a function of temperature shows the same trend with very similar absolute values with deviations typically less than 0.5% when comparing PEO from the micellar solution of Brij and from PEG solution, both in H_2O . As already mentioned, the difference in local density between the two systems can probably account for the observed difference. We note further

that the values for micellar solutions depend on values of the molar mass of the two PEO blocks used, which have a rather large difference in PEO block sizes. They are therefore less precise.

Finally, in Figure 1d, we have assembled data of the apparent specific volume of PEO as a function of temperature originating from various publications, which we compare with our own experimental results. Compared to the large spread of data found in the literature, the difference observed between dissolved and micellar PEO chains is negligible. However, these large discrepancies show clearly the importance of performing density measurements on exactly the system one is interested in, and that it is not possible to use values obtained under different conditions. The data from Mai et al.¹¹ correspond to a methyl-ended serie of PEO with different molar mass in the melt state. The extrapolated values at infinite chain length coincide with values obtained independently by Aucouturier et al.¹² for a PEG300 polymer in the melt state. We have commented on these results in the Introduction. More similar are the data obtained in water solution, but unfortunately they are sparse in the literature. The data from Armstrong et al.¹⁶ have been calculated from their measurements of specific volume on different Pluronics between 20 and 80 °C, in the same way as we do with the two Brij copolymers. This leads to much lower values of PEO than ours, but since this procedure is quite imprecise due to the uncertainty involved in reading the data from plots and uncertainty in the compositions of the Pluronics, we consider them less reliable. The data from Müller et al.¹³ correspond to density measurements in a large range of concentration at four different temperatures. To deduce the plotted values, we used the lowest available concentration of 10%. These values deviate significantly from our PEG4600 values, but this can most probably be attributed to the difference in molar mass. Even if the effect of molar mass on the specific volume of PEO is rather small, there is a tendency of decreasing values with increasing chain size, as a consequence of the relative decreasing influence of the end hydroxyl groups. In the same paper,¹³ values for two larger PEGs (with mass 2000 and 10000) at a temperature of 55 °C show that our corresponding value would lie just between them, as expected. The last set showed in Figure 1d are data from Wen et al.¹⁵ which are values of the specific volume of PEO of unspecified mass at a concentration of 5%. Despite the limited temperature range, the good agreement with our PEG4600 data supports their validity.

As already mentioned in the Introduction, the temperature variation of the apparent partial specific volume and of the solvent has a pronounced influence on data recorded by SAXS. Figure 2a shows the data for PEG4600 at a concentration of 10 wt % as a function of temperature. The data have been recorded at the pinhole instrument, optimized for solution scattering, at the University of Aarhus.²⁰ The temperature has a pronounced effect on the results due to the change in solvent quality as well as the change in contrast. The sample is a semidilute polymer solution and the scattering is within the random-phase approximation given by²¹

$$I(q) = \frac{c}{M} \Delta\rho^2 V^2 \frac{P(q)}{1 + \nu P(q)} \quad (3)$$

where c is the polymer concentration, M is the polymer mass, $\Delta\rho$ is the scattering length density difference between the polymer and the solvent (also known as the contrast), V is the apparent polymer volume, $P(q)$ is the single chain form factor, and ν is a parameter that increases with increasing concentration and with increasing excluded volume strength. The parameter

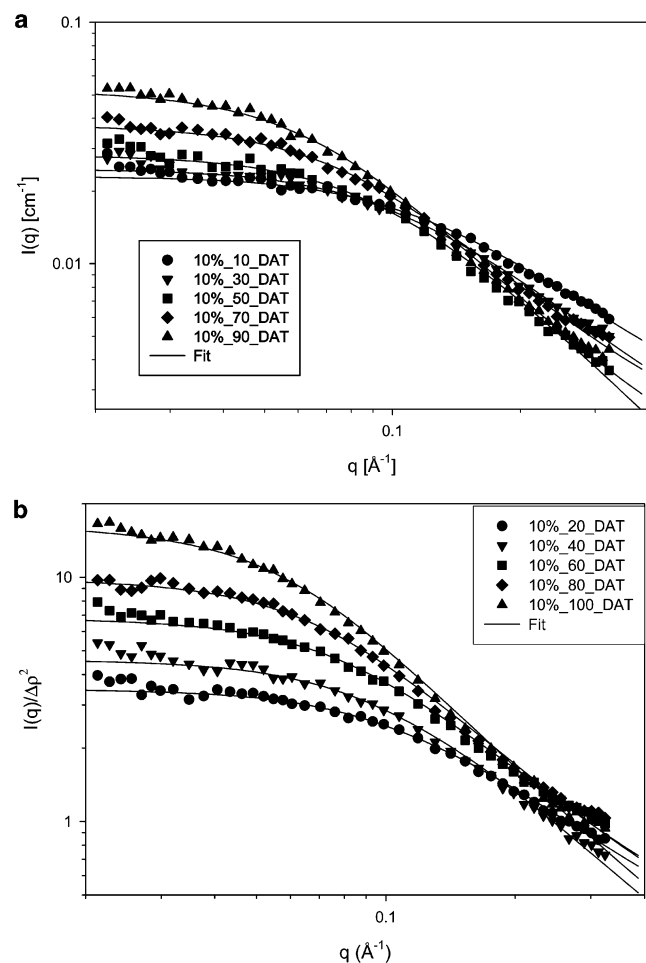


Figure 2. SAXS data for PEG4600 solutions of 10 wt % as a function of temperature with fits: 20 (circles), 40 (inverse triangles), 60 (squares), 80 (diamonds), and 100 °C (triangles). The full curves are fits using (3). In part a, the data are as recorded. In part b, the data are divided by the square of the excess electron density of the PEG chains to eliminate the influence of the change in contrast with temperature.

q is the modulus of the scattering vector. The $\Delta\rho$ is the scattering length density difference, which is the electron density difference multiplied by the classical Thomson radius of the electron. The electron density difference is calculated from the apparent specific density of the polymer and the bulk density of the solvent. The parameter ν decreases with increasing temperature as a result of the reduced solvent quality at higher temperatures.

Since $P(q)$ is a decreasing function for increasing q , the expression $P(q)/[1 + \nu P(q)]$ has the same q -dependence at high q . The fact that the data at different temperatures cross one another at around $q = 0.1 \text{ \AA}^{-1}$ is thus due to the changes in the contrast. In Figure 2b the same data are shown but divided by the square of the electron density difference. In this case the data at different temperatures do not cross and they show behavior in agreement with the expected theoretical behavior. There are some minor deviations between the various data sets at high q values, which are due to uncertainty in the background subtraction. After correction for the variation in the contrast term with temperature, the data show a much more pronounced temperature variation at low q . The curves in Figure 2 are fits using (3) with the form factor $P(q)$ of semi-flexible self-avoiding chains²² with a radius of gyration of $R_g = 26 \text{ \AA}$, as determined at low concentrations, where the concentration effects are vanishing. The form factor was the same for all temperatures and only ν and a parameter for describing the residual

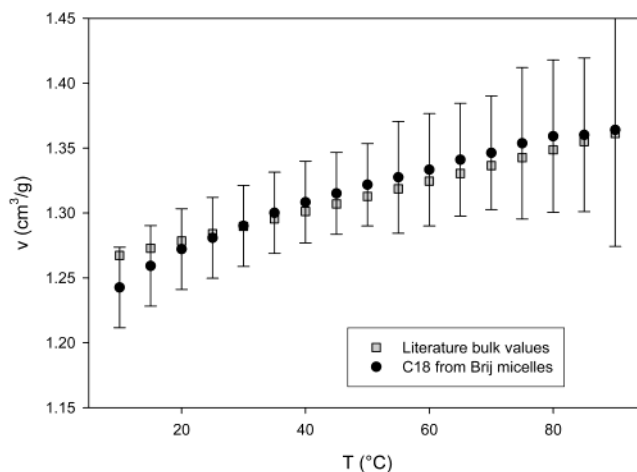


Figure 3. Apparent specific volume of octadecyl from Brij micelles compared with the bulk value for octadecane.

background were varied in the fit. The agreement between model and data is very good.

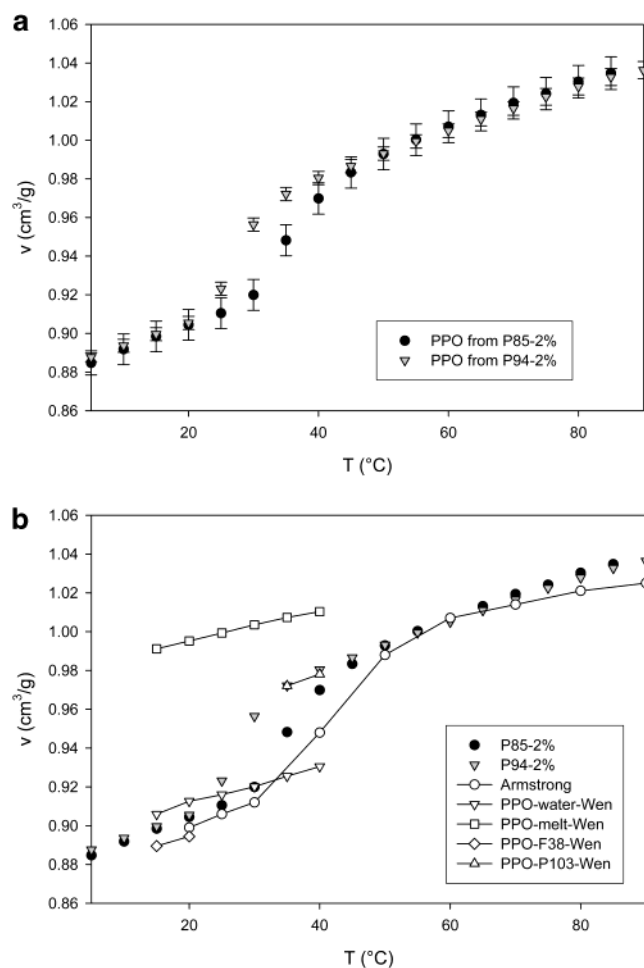
Octadecyl. Figure 3 shows the specific volume of the C18 octadecyl chain in the same temperature range, deduced from the measurements of the Brij micellar solutions. The error bars are much larger than those for the values of the PEO blocks, which are a consequence of the very low relative contribution of the C18 chain to the density of the measured solutions, directly related to its low contribution to the total weight of the block copolymers. The values correspond to the state of the hydrophobic core in the micelle, but since the conformation of the C18 chains and their possible interaction with the solvent and the PEO block is unknown, it is not obvious if they will behave as pure octadecane in the bulk state or not. Figure 3 shows that despite the relatively large uncertainty on the data, the values of C18 in the micellar core are very close to the values of pure octadecane¹⁸ and that the temperature dependence seems to be slightly more pronounced.

PPO. In Figure 4a the apparent specific volume of poly(propylene oxide) (PPO) as deduced from the two Pluronic solutions P94 and P85 is represented. Here, we have used the previously obtained PEO values from Brij solutions, as we expect the triblock copolymers P94 and P85 to form micelles in water, and the PEO chains to be in a corona structure similar to that of the Brij micelles. However, we also tried to use the values from PEG4600 in water, and this led to a negligible small difference in the calculated values. We observe an abrupt transition in the temperature dependence of the specific volume for both systems, which corresponds to the aggregation of the polymers and formation of micelles. This behavior has already been observed in previous studies of Pluronic. Wen et al.¹⁵ have done an extensive investigation of the effect of molar mass and relative PPO/PEO mass ratio. They found that the transition temperature decreases with increasing molar mass as well as with increasing PPO/PEO ratio.

Figure 4a shows that the transition occurs around 30 °C for P94 and 35 °C for P85. The molar mass of both polymers is about 4600 and the slightly higher molar mass of P94 probably does not explain the shift in the transition. However, the PPO/PEO mass ratios are quite different, namely 1.12 for P94 and 0.80 for P85. Thus the behavior is in accordance with a lower transition temperature for increasing PPO/PEO mass ratio. This behavior can be rationalized by the lower solvent quality of water for PPO than for PEO, which becomes even lower when the temperature is increased. PEO can be dissolved in water in the whole range of temperature (no transition is observed for

TABLE 1: Values of the Apparent Specific Volume (in cm³/g) for Octadecyl in the Micellar State, for PEO from Brij Micelles (5% in H₂O), for PEG4600 (average values), for PPO from P85 and P94 (2% in H₂O), and for PBO in the Micellar State (2% in H₂O)

T (°C)	octadecyl	PEO in the micellar state	PEO from homopolymer	PPO from P85	PPO from P94	PBO in the micellar state
5			0.8186	0.8847	0.8877	
10	1.243	0.8230	0.8240	0.8918	0.8936	1.000
15	1.259	0.8274	0.8291	0.8984	0.8996	1.009
20	1.272	0.8318	0.8337	0.9045	0.9054	1.016
25	1.281	0.8359	0.8383	0.9105	0.9231	1.022
30	1.290	0.8397	0.8426	0.9199	0.9564	1.030
35	1.300	0.8435	0.8469	0.9482	0.9721	1.036
40	1.308	0.8477	0.8511	0.9699	0.9804	1.042
45	1.315	0.8520	0.8553	0.9833	0.9866	1.051
50	1.322	0.8561	0.8595	0.9929	0.9931	1.053
55	1.328	0.8604	0.8636	1.0002	0.9994	1.059
60	1.333	0.8646	0.8678	1.0070	1.0049	1.066
65	1.341	0.8689	0.8720	1.0131	1.0110	1.068
70	1.346	0.8733	0.8762	1.0193	1.0165	1.074
75	1.354	0.8778	0.8806	1.0242	1.0225	1.080
80	1.359	0.8824	0.8849	1.0303	1.0278	1.085
85	1.360	0.8870	0.8893	1.0348	1.0327	1.090
90	1.364	0.8917	0.8934	1.0250	1.0363	1.096

**Figure 4.** (a) Apparent specific volume of PPO from P85 and P94 block copolymer solutions at 2% in H₂O. (b) Apparent specific volume of PPO: comparison between previous literature data and results from this study.

PEG4600 in water). The increase in specific volume is due to the more oily nature of the PPO micellar core and the poorer packing when the PPO becomes less solvated. We note a very good agreement between the two Pluronics for values of the specific volume below and above the transition temperature, as expected.

In Figure 4b, we compare our experimental data with previous literature results on PPO under different conditions.^{15,16} The specific volume of PPO below the transition temperature should be close to the values of PPO in water, since the polymers are in a nonaggregated state; this is quite well verified. Some data obtained from solutions of Pluronics (F38 in the nonaggregated state and P103 in the micellar state) show a reasonably good agreement with our data, but unfortunately the data are only available in a restricted temperature range. PPO bulk values are also shown and are clearly much higher than the values in the aggregate state. This suggests that PPO in the core of micelles is far from being desolvated, contrary to the C18 chains in Brij micelles. The core contains some water in agreement with the conclusion already drawn by Wen et al.¹⁵ and in accordance with small-angle neutron scattering data on P85,²³ where a volume fraction of 40% of water in the core was found. Data from Armstrong et al.¹⁶ shown in Figure 4b have been deduced together with the PEO data in Figure 1d. They were obtained by using data from Pluronics with molar masses between 1750 and 2250 and PPO/PEO mass ratios between 0.24 and 2.69. As previously discussed, they are not very reliable, but despite this fact and the different nature of the Pluronics used, they are still of the right magnitude.

PBO. Figure 5 represent the data for poly(butylene oxide) (PBO), from measurements on the block copolymer (EO)₉₂-(BO)₁₈ in water. This polymer has a molar mass around 5300 and a PBO/PEO mass ratio of 0.32. Note that the error bars are quite large, due to the difficulty of obtaining highly reproducible data with solutions of this polymer. We observe a slight change of the shape of the curve at a temperature close to 35 °C, which is related to the dehydration of the PBO in the micellar cores.²⁴ Due to the high hydrophobicity of the PBO, we expect the core of the micelles to contain less water than the PPO cores, which means that the specific volumes above the transition temperature should be close to the bulk value. The values determined by Mai et al.¹¹ for PBO in the melt state are indeed very comparable for BO4800 and infinite length PBO; however, the temperature dependence is more pronounced for PBO in the micellar state.

Hydration. The results for the specific volumes of PEO/PEG, PPO, and PBO in water display some general trends. In the fully hydrated state, PEO and PPO have much smaller specific volumes than in the melt. In the partially dehydrated states of the micellar cores, PPO and PBO have specific volumes, which

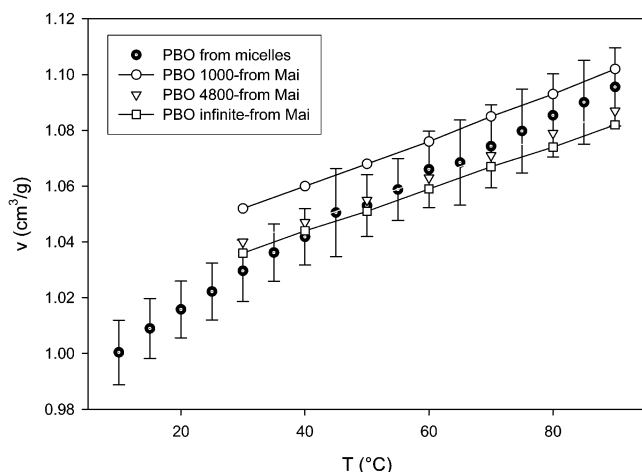


Figure 5. Apparent specific volume of PBO in the micellar state (2% in H₂O) and comparison with literature bulk values.

are much larger and closer to the melt values. This indicates that there is a large perturbation of the water in the vicinity of the polymer chains for fully dissolved polymers. Molecular dynamics (MD) simulations by Smith and Bedrov²⁵ demonstrate a very strong hydrogen-bonding interaction between the water and the two lone pairs of oxygen atoms in the backbone of the water. For *trans-gauche-trans* (*tgt*) conformations, a water molecule can make hydrogen bonds with two oxygens in neighboring repeat units. This bonding is believed to be the origin of the relatively large negative excess volume of PEO in water. As the temperature is increased the bonded water molecules become more disordered and the solvent quality effectively becomes poorer. The temperature dependence of the specific volume for PEO in solution and in the melt is significantly different. The data in Figure 1 suggest that in the melt there is a 5% increase in volume between 10 and 90 °C, whereas the solutions have a significantly larger change of about 7%. The difference in the temperature dependence is most probably due to the disordering of the water.

PPO in water can form similar strong hydrogen bonds with the oxygen atoms of the polymer backbone. At low temperature before the micelle formation, PPO of the Pluronics has a similar large negative excess volume, which has the same origin as the negative excess volume of PEO. When the micelle formation occurs, the strongly bound water of the PPO disappear and the remaining water in the core is in a more disorder state with an associated higher volume. The MD simulations by Bedrov and Smith²⁶ suggest that the water at high polymer concentration is involved in bridging between different polymers and that this gives a smaller excess volume than at low concentration.

PBO-PEO block copolymers in water form micelles even at low temperatures.^{24,27} Recent SANS investigations^{27,28} show that the water content of the PBO core decreases from about 55 vol % at room temperature to about 40 vol % at 75 °C. This cooperates nicely with the relatively large change in apparent partial specific volume of the PBO as shown in Figure 5.

Recently Stieger, Pedersen, and Richtering²⁹ have in connection with SANS studies investigated the partial specific density of microgels of PNIPAM (poly(*N*-isopropylacrylamide)). The microgels are thermo-sensitive and have a collapse transition at 33 °C. At low temperature the gels are hydrated with a polymer volume fraction of about 10%, and above the transition, the polymer volume fraction increases to about 40%. The density measurements show a change of partial specific volume at the transition, which is very similar to that of PPO in Pluronics when micelles are formed. The specific volume

increases by about 2–3% at the transition in a quite narrow temperature range. The amide group of the PNIPAM polymer forms strong hydrogen bonds with the surrounding water and it is the partial dehydration of the amide group at the transition that leads to the large density change. Recent partial specific density measurements on microgels of poly(*N*-isopropylmethacrylamide) (PNIPMAM) show a similar transition around 45 °C also with a 3% change at the transition.³⁰

Conclusions

The apparent specific volume of poly(ethylene oxide), poly(propylene oxide), poly(butylene oxide), and octadecyl in the micellar state as a function of temperature has been determined by using a highly precise densitometer DMA 5000 from Anton Paar in a very broad temperature range. The primary purpose of the study has been to provide information that can be used for calculating contrast factors for SAXS modeling. However, the results are not only very useful for this, but they also deliver information on the effect of isotope (D₂O/H₂O), solute concentration, and the aggregation behavior of Pluronics and of the PBO-PEO block copolymer. As shown in various plots, data presented in the literature are rather incomplete or are restricted to conditions quite different from those present in the micellar state. The results in the present paper with an extensive temperature variation thus fill a gap in the literature.

For PEO and PPO, the apparent partial specific volume in water in the low-temperature state is quite low compared to the specific volume in the melt. This can be associated with water molecules making strong hydrogen bonds with the oxygen atoms on the polymer backbone. As these water molecules become gradually more disordered when the temperature is increased, the polymer apparent specific volume increases. A pronounced temperature dependence with the same origin is also displayed for PBO in the micellar cores of PBO-PEO block copolymers and in PNIPAM and PNIPMAM microgels.

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