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ORIGINAL CONTRIBUTION

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PGSE-NMR studies of solvent diffusion in poly(*N*-isopropylacrylamide) colloidal microgels

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Abstract The solvent self-diffusion coefficient has been studied in thermoshrinking poly(*N*-isopropyl acrylamide) microgel dispersions by the pulsed-gradient spin-echo PGSE-NMR technique, as a function of temperature and mass fraction. After suitable corrections for the temperature, the H_2O/D_2O ratio and the relative volume fractions, all the self-diffusion data obtained over a temperature range of approximately 40 °C and mass fraction (2–12 % wt/wt) could be superimposed with the volume fraction as the universal factor. The observed reduction in the solvent self-diffusion coefficient with volume fraction was greater than that predicted by simple obstruction theory. After correction for-, and the subsequent removal of the obstruction effect, the diffusion of the solvent through the core of the particle is elucidated. As found for other polymer-solvent systems, there were no specific binding effects. The diffusion of the solvent in these dispersions over such temperature and mass fraction ranges could be rationalised assuming a constant solvent self-diffusion coefficient in the core of the particles.

Key words NMR diffusion – solvent diffusion – hydrogels – microgels – temperature

Introduction

In recent years, there has developed a need for more efficient processing technologies such as targeted drug delivery or enhanced oil recovery [1]. In the former case, any treatment involving the use of drugs is far more effective if the active compound can be delivered only to the required location. This will allow the use of lower doses and concomitantly reduce any adverse side-effects caused by the drug. Polymeric "vehicles" are increasingly having a role to play in these advances – most drugs typically have low solubilities in water, a rather significant factor given the water content of the body. Drugs are, therefore, "formulated" to have the correct solubility characteristics within a suspended medium. This does not always lead to an appealing product as the often "chalky" nature of some tablets testifies. Fortunately, these media are being replaced by polymeric gels which are more palatable. Polymers are also being used as water soluble capsules which slowly dissolve to release the encapsulated drug at a controlled rate. However, there is an emerging class of colloidal particles called hydrogels, which may become important to this, as well as other similar applications.

Hydrogels, more commonly called microgels, have received considerable attention in the recent literature [2] due to their peculiar temperature characteristics. Three types of phase transitions can be identified [3]; thermoswelling (where there is an increase in size of the particles with increasing temperature), thermoshrinking and a "convexo" type which is a combination of both expansion and contraction with temperature. The size-temperature profile for a thermoshrinking microgel is a result of an increase in the Flory parameter, χ, which defines the interaction between the solvent and the polymer segments. As χ increases with temperature, the segment–solvent interaction becomes less favourable and hence, more segment-segment interactions are induced. This process is facilitated by the particle shrinking, thereby forcing the solvent out of the interstitial spaces. The size-temperature profile is completely reversible. Small organic molecules, such as drugs, and heavy metal ions can be "stored" in the core of the particle at lower temperatures and released as the microgel shrinks on heating. Approximately 80% of the carried material may be recovered and the process repeated. The transition from expanded to contracted occurs [4] at about 35 °C.

The structure of the core of the poly(*N*-isopropylacrylamide) microgel is believed to be rather "sponge-like" at low temperatures but much more compact at higher temperatures although their adsorption characteristics are similar to the widely studied polystyrene latex [5].

Pyrene and ruthenium tribispyridine have been used as probes to study, by photophysical methods, the internal structure of the core [6]. The idea is to introduce a probe molecule to the core of the particle whose spectral characteristics will be representative of the nature of its environment. It is tacitly assumed in those sorts of study that the inclusion of the probe has little effect on the microgel itself. At low temperatures, when the microgel is fully hydrophilic, the fluorescent and quencher molecules are predominantly located in the aqueous phase. With increasing temperature, the gel becomes more hydrophobic and the fluorescent molecules are absorbed. Approximately 76% of the fluorescent molecules are located in the core of the microgel. However, there is also another "probe" molecule present in the system that can be used much more easily to study the nature of the microgel dispersions – the solvent itself.

In this paper, we present solvent diffusion studies of the microgel dispersions as a function of both mass fraction and temperature as measured by the pulsed-gradient NMR method (PGSE-NMR). In the last 10 years, solvent diffusion studies by the PGSE-NMR technique have become one of the more important methods for studying surfactant and colloidal systems [7–9]. The principle reasons for this are that the diffusion coefficient – and especially the self-diffusion coefficient as measured by PGSE-NMR – is easy to measure and to interpret, and that no special chemistry is involved (merely that the molecule under observation contains hydrogen). Perhaps most important is the advantage that the technique is chemically selective so that, in a single experiment, the diffusion coefficient of each species in a multi-component system may be measured simultaneously. The applicability of PGSE-NMR to study these sorts of systems has been demonstrated through solvent self-diffusion measurements in a range of microemulsion and surfactant systems [7, 9–11].

The solvent self-diffusion coefficient in colloidal solutions has been studied extensively and, in general, two effects are observed [12]. First, an "obstruction effect" arises from the increase in the diffusion pathlength because the solvent molecules must now diffuse around the relatively massive, suspended phase. Second, a "hydration effect" arises through specific interactions between the solvent and segment species which further affect the translational and rotational motion of the solvent molecules. The aim of these sorts of studies is an attempt to extract information, such as solvation numbers, on the molecular interactions between the dispersed and continuous media. In order to do that, a theoretical estimate of the obstruction effect is required. This correction is non-trivial since the obstruction effect is dependent on the shape and size of the obstructing particles which are neither ordered nor randomly dispersed throughout the continuous medium. To further complicate matters, these particles are also mobile, but generally to a much smaller degree.

Many predictions for the form of this obstruction have been proposed but the Maxwell–Fricke mixture theory [13] appears to closely predict the diffusion behaviour observed in suspensions of impenetrable, spherical particles which are expected to show little or no hydration effect;

$$(1 - p_{\mathrm{comp}})D_s/D_o = (1 - p)/(1 + p/2) , \quad (1)$$

where p_{comp} is the volume fraction of suspended phase, p is the volume fraction of suspended phase plus tightly bound solvent, D_s is the measured solvent diffusion coefficient and D_o is the self-diffusion coefficient of the pure solvent. The Maxwell–Fricke mixture theory is strictly only applicable for the case of dilute, impenetrable spheres and then only to the first order in p although it has been shown to be a good approximation for more concentrated dispersions provided the diffusion coefficient of the suspended phase is low [14]. The isotropic diffusion coefficient (as implied by Eq. (4) below) in the PGSE-NMR technique assumes that Fick's law is being obeyed. However, since the volume fraction p_{comp} is inaccessible to the bulk solvent, the effective diffusion coefficient that is measured is not the self-diffusion coefficient in the continuous medium. To account for this, Eq. (1) contains a factor $(1 - p_{\mathrm{comp}})$ which corrects the data to "constant volume". For the case of negligible solvent binding, $p = p_{\mathrm{comp}}$, (i.e. no hydration effects) Eq. (1) may be simplified:

$$D_s/D_o = 1/(1 + p/2) \quad (2)$$

The diffusion of water in silica and polystyrene latex dispersions has been shown to follow Eq. (2) highlighting the need for this correction.

In contrast, solvent diffusion measurements in microemulsions do not exhibit this behaviour – the diffusion coefficients being much slower than that predicted by this simple argument [15]. This extra reduction arises through the hydration effect. Similar behaviour has been observed in biological systems [16] where a simple two-state mobility model has been invoked which permits an estimate of the level of hydration to be obtained. For the case of polymeric gels, a chemical interaction with the solvent, such as hydrogen bonding, was also found to affect the translational and rotational motion of the solvent molecules [15, 17]. However, for the case of concentrated polymer solutions, the Maxwell–Fricke model is often used but tends to neglect the subtleties in the data [18]. In these cases, a modified Enskog theory or a description based on the free volume of the system [18, 19] is found to be a slightly better representation for the data. Both of these theories are, however, much more complicated than the simple Maxwell–Fricke model.

A more general theory has been proposed by Jönsson et al., based on a cell model for simple liquid diffusion [20]. This approach has been very successful in describing systems containing highly-charged particles of various shapes over a wide concentration range as well as the self-diffusion of counterions. The authors argue that this model is applicable for describing the self-diffusion of small molecules in colloidal and locally heterogeneous systems in general. Indeed, one of us has used a variation of this model to estimate the average volume fraction of a polymer layer adsorbed onto colloidal silica [21]. Using the formalism of irreversible thermodynamics, global and localised diffusional flows, based on Fick's law, are calculated from representative average concentration gradients. Inherent in this calculation is the need for the $(1 - p_{\mathrm{comp}})$ correction.

For the simplest case of monodisperse, spherical obstructing particles in a spherical-cell model, the effective self-diffusion coefficient is given by;

$$D_s^{\mathrm{eff}}/D_o = 1/(1 + \phi/2)\,, \tag{3}$$

which is equivalent to Eq. (2) since the $(1 - p_{\mathrm{comp}})$ correction is implicit in the deviation. For other shapes, however, the derivation is quite different.

Within this framework, the present study was initiated – given the temperature dependent nature of the interaction between the polymer segments comprising the microgel and the solvent, a hydration effect may be expected dependent on the temperature. Similarly, if the particle behaves more like a "sponge," the solvent diffusion behaviour may have a contribution from the solvent in the core of the microgel which would have similarities to a polymer solution.

Experimental; samples

The thermosensitive colloidal microgel particles of poly (*N*-isopropylacrylamide), poly(NIPAM), have been prepared by a free-radical, emulsion polymerisation of NIPAM in H_2O at 70 °C using *N,N'*-methylene-bis-acrylamide (BDH Chemicals) as the cross-linking agent and ammonium persulphate as the initiator under a nitrogen atmosphere as described by the procedure of Pelton and Chibante [22]. The microgels were extensively dialysed against distilled water prior to further study. The dialysed microgel solution had a mass fraction of approximately 0.4 % wt/wt and was concentrated by repeated centrifugation from H_2O/D_2O solutions to a final particle concentration of 12.5 % wt/wt. High-resolution ^{1}H NMR studies suggest the final H_2O concentration of this stock solution to be approximately 7.5% wt/wt. All subsequent dispersions were prepared by dilution of the stock solution with D_2O.

Experimental; NMR measurements

For isotropic Brownian motion [23], the self-diffusion coefficient, D_s, is extracted by fitting to Eq. (4), the measured peak integral, $A(\delta)$, as a function of field gradient duration, δ, intensity, G, separation, Δ, and of rf pulse interval, τ,

$$A(\delta) = A(o)\exp(-2\tau/T_2)\exp[-\gamma^2\delta^2G^2(\Delta - \delta/3)D_s]\,, \tag{4}$$

where γ is the magnetogyric ratio of nucleus under observation, in this case, protons. The $A(o)$ term is determined by the number of protons in the sample and the first exponential term is the attenuation from spin-spin relaxation during the duration of the experiment.

When both the duration and intensity of the field gradients have been varied in a single experiment, Eq. (4) is often re-written as

$$A(\delta) = A'(o)\exp[-kD_s]\,, \tag{5}$$

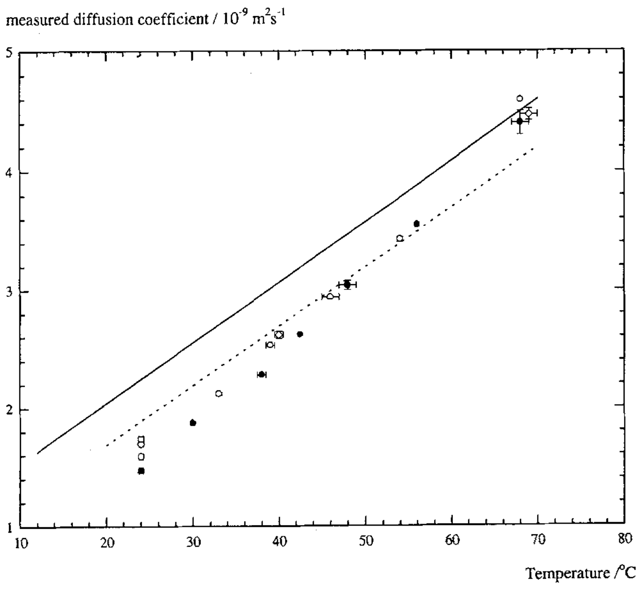
where $k = \gamma^2\delta^2G^2(\Delta - \delta/3)$. Hence, a plot of $A(\delta)$ vs k should be exponential with a time constant equal to the self-diffusion coefficient.

The PGSE measurements were performed on a JEOL FX100 high-resolution NMR spectrometer employing a Hahn echo sequence. The spectrometer is equipped with a Woodward gradient amplifier [24] which delivers pairs of read and write gradients matched to better than 10 ppm. Three field gradient prepulses were applied before every scan to bring the effects of coil heating and eddy currents to a first order steady state. The gradient amplifier was calibrated with a sample of known diffusivity, water, giving a field gradient of $G = 0.060$ *T/m*. The gradient pulse interval, Δ, was fixed at 100 ms and δ varied between 0.5 ms and 9.5 ms in 0.5 ms intervals.

Results and discussion

Poly(NIPAM) microgels are thermoshrinking, so suitable combinations of mass fraction and temperature can, in principle, result in a similar volume fraction. Fig. 1 shows the measured solvent diffusion coefficient as a function of temperature for three different mass fractions. This diffusion coefficient is not the continuous phase self-diffusion coefficient since the data have not yet been corrected for the volume fraction of the particles. Hence, it is merely called a "diffusion coefficient". As can be seen, the measured solvent diffusion coefficient depends on both temperature and mass fraction. Also shown is the variation of the self-diffusion coefficient with temperature for pure D_2O and H_2O. With increasing temperature, the measured solvent diffusion coefficient approaches that of the pure solvent as a result of the particle shrinking, thereby reducing the **volume** of the obstructing species. At a given temperature i.e. fixed particle size, the measured solvent diffusion coefficient decreases with increasing mass fraction as a result of an increase in the **number** of obstructing species. With increasing temperature, the effect of the **number** of obstructing species also decreases due to their smaller size. At the high temperature limit, the measured solvent diffusion coefficient closely agrees with the extrapolated pure H_2O value – rather surprising given the low concentration of the H_2O in the dispersion. The presence of convection currents at this temperature cannot be ruled out so these three points must be used with some caution.

Fig. 1 The measured solvent diffusion coefficient as a function of temperature for poly (NIPAM) dispersions of mass fractions 12 % wt (solid circles), 8 % wt (open circles), 4 % wt (diamonds) and 2 % wt (open squares). The solid and dotted lines correspond to the temperature dependence of the self-diffusion coefficient of pure H_2O in H_2O and trace H_2O in D_2O respectively



As discussed previously, the data must be corrected for the relative volume fraction of the particles using the $(1 - p_{\text{comp}})$ factor. This is not a trivial procedure in these systems, since by virtue of the temperature vs. volume fraction and mass fraction vs. volume fraction dependencies, **every measurement** has a different volume fraction. A knowledge of the particle size as a function of temperature is therefore required. At low temperatures, where the particles have attained their maximum size, the particle number concentration may be calculated knowing the mass fraction and density of the particles. Having obtained the number concentration of the particles and using the size vs. temperature behaviour, it is then possible to calculate the volume fraction for each pair of temperature and mass fraction parameters.

A further correction must be applied to this data – the diffusion of H_2O in H_2O is faster than the diffusion of trace H_2O in D_2O as shown by the lines drawn in Fig. 1. Fortunately, this correction factor is linear in H/D volume ratio [25]. Figure 2 shows the solvent self-diffusion coefficient corrected for the relative volume fraction $(1 - p_{\text{comp}})$ and H/D ratio (*) as a function of volume fraction for the lowest temperature studied, 24 °C. Henceforth,this **self**-diffusion coefficient will be called the "corrected diffusion coefficient"; $(1 - p_{\text{comp}})D_s^*$. As may be seen, there is a linear relationship between the effect of the microgel particles on the corrected diffusion coefficient and their volume fraction. The intercept at zero volume fraction is close to the theoretical value for the diffusion of trace H_2O in D_2O adding some weight to the two correction factors applied to the data.

In all cases studied, a single diffusion coefficient fit (Eq. (5) described the attenuation function within experimental error. Non-linearity in the attenuation function would arise through the presence of a distribution of diffusion rates. For the case of a "spongy" particle, one might expect that the solvent in the core of the particle would have a different self-diffusion coefficient than the solvent comprising the continuous medium. However, if the exchange rate between the core and the continuous medium is fast on the NMR timescale, a spatially- and time-averaged diffusion coefficient would be monitored which would not exhibit non-linearity in the attenuation function. In that

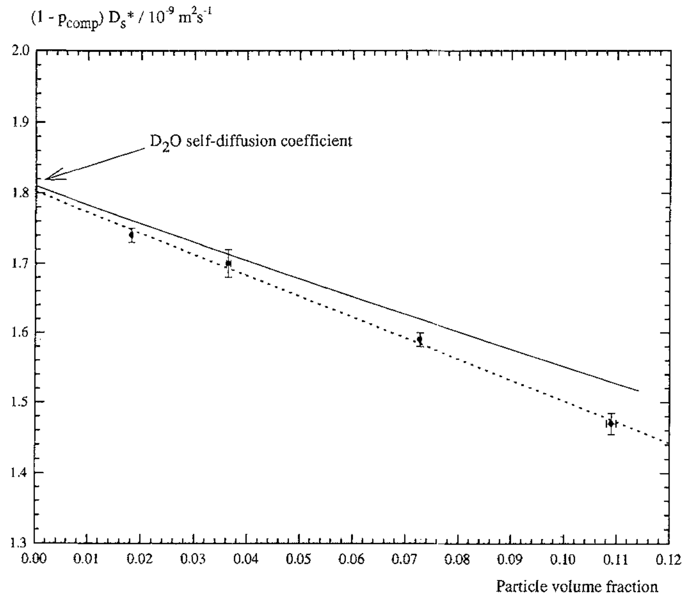


Fig. 2 The corrected solvent self-diffusion coefficient as a function of volume fraction for poly (NIPAM) dispersions at 24 °C. The dotted line is simply a linear fit to guide the eye. Also shown is the theoretical value for the diffusion of trace H_2O in D_2O at this temperature and the theoretical prediction of the Jönsson obstruction effect (solid line)

case, the average self-diffusion coefficient follows;

$$D_s(\mathrm{av}) = p^{\mathrm{fast}} . D_s^{\mathrm{fast}} + (1 - p_{\mathrm{fast}}) . D_s^{\mathrm{slow}} , \tag{6}$$

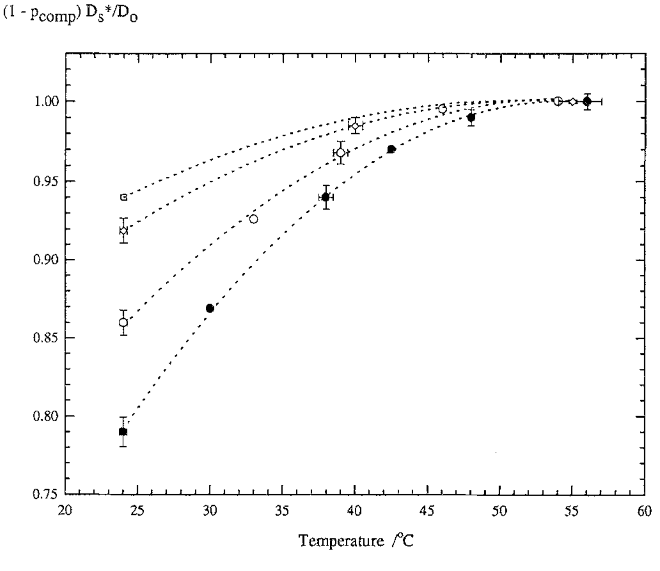
where p^{fast} is the fraction of species with a diffusion coefficient D_s^{fast} and D_s^{slow} is the diffusion coefficient of the slower species. For the case described here, D_s^{fast} would correspond to the continuous phase self-diffusion coefficient whereas any solvent in the core of the particle would be represented by D_s^{slow}. With increasing volume fraction, one would expect $(1 - p_{\mathrm{fast}})$ to increase if there is solvent in the core of the microgel.

In these thermoshrinking systems, a reduction in the solvent self-diffusion coefficient may arise through two mechanisms: firstly, due to the presence of the slower diffusion of the solvent through the core of the particles, and secondly, due to the increased diffusion pathlength of the solvent molecules caused by the presence of the relatively massive particles i.e. the obstruction effect. It is important to realise the relative magnitudes of these two effects.

The solid line in Fig. 2 shows the theoretical prediction based on the obstruction theory of Jönsson et al. As may be seen, this theory does not adequately describe this data, although it is very successful in describing similar data for "solid" particles. Therefore, this extra reduction in the corrected diffusion coefficient is ascribed to be due to more slowly diffusing solvent in the core of the particles. In order to extract useful information on the solvent in this environment, it is necessary to correct the data for the obstruction effect. Hence, we shall investigate the obstruction effect first.

The correction factors discussed above have, therefore, been applied to all the data shown in Fig. 1. Essentially, these corrections do not alter the observed behaviour but significantly enhance the effect of the presence of the microgel particles. To further emphasise the presence of the microgel particles, it is possible to remove the temperature dependence of the diffusion coefficient by dividing each value of the corrected diffusion coefficient by the theoretical solvent self-diffusion coefficient at that temperature. This factor, hereon called the "relative diffusion coefficient", is shown in Fig. 3 as a function of temperature. The reduction in the diffusion rate quantified by the relative diffusion coefficient arises purely from the obstruction effect and the diffusion of the solvent in the core of the particles. As may be seen, the effect increases with an increase in the particle number concentration at a given temperature and decreases with increasing temperature. The mass fraction dependence of this effect also decreases with increasing temperature. Note that the high temperature data points have been omitted. These trends are reminiscent of the volume fraction dependence on temperature and mass fraction. Accordingly, the relative diffusion coefficient vs. temperature data of Fig. 3 have been replotted in Fig. 4 as function of volume fraction. The data which covers a temperature range of approximately 30 °C

Fig. 3 The relative diffusion coefficient as a function of temperature for poly (NIPAM) dispersions of mass fractions 12 %wt (solid circles), 8 %wt (open circles), 4 %wt (open diamonds) and 2 %wt (open squares)



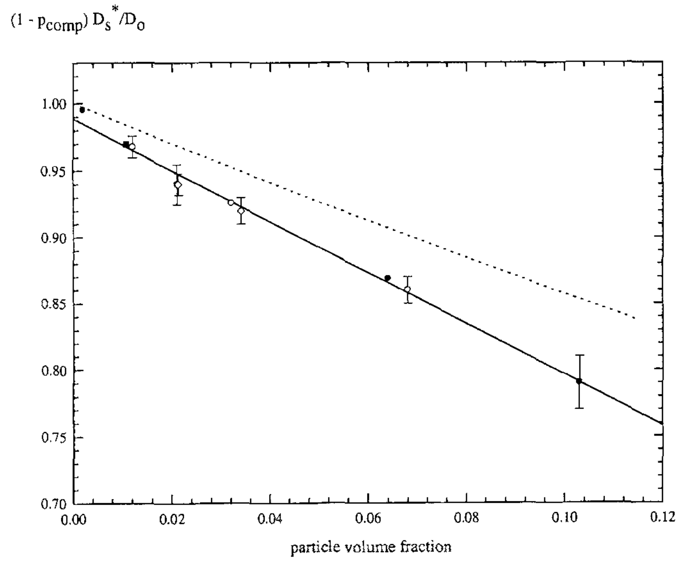


Fig. 4 The relative diffusion coefficient as a function of volume fraction for poly (NIPAM) dispersions for all mass fractions and temperatures. The dotted line corresponds to the theoretical behaviour as predicted by the Jönsson obstruction effect

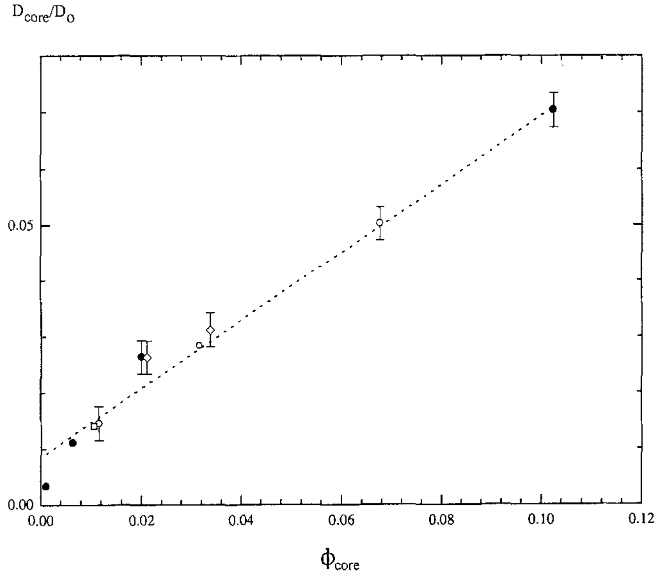


Fig. 5 The contribution to the observed relative diffusion coefficient from solvent in the core of the microgels as a function of core solvent volume fraction at mass fractions of 12 % wt (closed circles), 8 %wt (open circles), 4 % wt (open diamonds) and 2 % data (open squares)

and four mass fractions shows surprisingly good agreement given the number and type of corrections that have had to be applied to the data. There appears to be a generalised behaviour of the relative diffusion coefficient with the volume fraction as the universal factor. Also shown is the prediction from the Jönsson et al. obstruction theory (dotted line).

The Jönsson et al. prediction underestimates the observed reduction in the relative diffusion coefficient but the data and the prediction do converge to a common point at zero volume fraction. This extra reduction is ascribed to the solvent diffusing in the core of the microgel particles with a slower diffusion coefficient. A simple two-state mobility model can be used to extract information on the solvent in the core characterised by a self-diffusion coefficient, D_{core};

$$\frac{(1-p_{\text{comp}})D_s}{D_o} - \frac{(1-p_{\text{comp}})}{\left(1+\frac{\phi}{2}\right)} = \frac{\phi_{\text{core}}D_{\text{core}}}{D_o}, \qquad (7)$$

where the first term corresponds to the experimental, relative diffusion coefficient and the second is the theoretical, obstruction effect proposed by Eq. (3) – the difference being due to the diffusion of the solvent in the core of the microgel particles.

Knowing the size of the particles as a function of temperature allows their volume at any temperature to be calculated. It is assumed that as the particles increase in size due to the decreasing temperature, the change in the particle volume is equal to the volume of solvent that is taken up i.e. the change in the particle volume from its fully compact state (higher temperatures) to the swollen state gives the volume of solvent that is present in the core of the particles. Hence, it is possible to calculate ϕ_{core}. The term describing the diffusion of the solvent in the core of the particles need not be corrected for the obstruction effect and therefore, this correction has been removed – the increase in the diffusion pathlength caused by the solvent diffusing around the particle does not effect the solvent diffusing through the core of the particle. A simple dependence of the relative diffusion coefficient on ϕ_{core} is observed as shown by Fig. 5. Since these volume fractions have in fact been obtained from combinations of different mass fractions and temperatures, the lack of any discontinuity confirms the assumption that there is indeed no specific binding due to any temperature effects. A discontinuity at the lowest volume fractions studied (corresponding to the highest temperatures and largest mass fractions) might be present where perhaps the assumption of a constant core self-diffusion coefficient may break down. The slope of the line, 0.60 (± 0.05) drawn in Fig. 5 corresponds to the relative diffusion coefficient in the core. Interestingly, the values of ϕ_{core} and ϕ thus calculated are very similar, suggesting that the microgel has a very open structure. The relative diffusion coefficient of the solvent in the core of the particles is approximately a factor of 2 slower than the bulk phase.

Conclusions

The solvent self-diffusion coefficient in aqueous dispersions of thermoshrinking poly(NIPAM) particles has been studied as a function of particle mass fraction and temperature. It is shown that effects originating from the temperature and mass fraction dependencies on the volume fraction of the particles is sufficient to describe the observed diffusion behaviour. After correction for the relative volume fractions, the H/D ratio of the solvent and the temperature, the diffusion coefficient of the solvent in the core of the particles could be obtained. At higher temperatures where the poly(NIPAM) particles .are hydrophobic, a simple obstruction theory is sufficient to explain the diffusion data. At lower temperatures, this obstruction theory no longer describes the diffusion data, the solvent having a self-diffusion coefficient lower than that predicted. This reduction in the solvent self-diffusion coefficient is analysed in terms of solvent diffusing in the core of the particles. No specific binding effects were observed – the observed effects could be simply rationalised by the volume fraction of the solvent in the core of the particles. An estimate of the self-diffusion coefficient of the solvent in the core is obtained which is a factor of 2 slower than the bulk phase value, suggesting that there is a significant interaction between the solvent and the microgel core.

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References

1. Snowden MJ, Vincent B, Morgan JC (1993) UK Patent GB2262117a
2. Snowden MJ, Vincent B (1992) Chem Commun 1103
3. Otake K, Inomata H, Konno M, Saito S (1990) Macromolecules 23:283
4. Snowden MJ, Murray M, Friduddin R, Ihtshamul H, Cook J, Chowdhry BZ (1994) Chem Commun (submitted:)
5. Tam KC, Ragaram S, Pelton RH (1994) Langmuir 10:418
6. Pankasem S, Thomas JK, Snowden MJ, Vincent B (1994) Langmuir submitted:
7. Stilbs P (1987) Prog Nucl Magn Reson Spectrosc 19:1
8. Stilbs P (1994) Solubility in Surfactant Aggregates (Surfactant Science Series) Christian D, Scamehorn JF Marcel Dekker, Inc.. New York
9. Söderman O, Stilbs P (1994) Prog Nucl Magn Reson Spectrosc 26:445
10. Stilbs P, Lindman B (1984) Prog Colloid Polym Sci 69:39
11. Lindman B, Stilbs P (1987) Microemulsions: Struct. Dyn., 119–52. Edited by: Friberg, Stig E.; Bothorel, Pierre. CRC: Boca Raton, Fla.
12. Von Meerwall E, Mahoney D, Iannacchione G, Skowronski D (1990) J Colloid Interface Sci 139:437
13. Cheever E, Blum FD, Foster KR, Mackay RA (1985) J Colloid Interface Sci 104:121
14. Chiew YC, Glandt ED (1983) J Colloid Interface Sci 94:90
15. Muhr AH, Blanshard JM (1982) Polymer 23:1012
16. Beall PT (1983) Cryobiology 20:324
17. Lauffer MA (1961) J Biophys 1:205
18. Waggoner RA, Blum FD, Macelroy JMD (1993) Macromolecules 26:6841
19. Macelroy JMD, Kelly JJ (1985) AIChE J 31:35
20. Jönsson B, Wennerström H, Nilsson PG, Linse P (1986) Colloid Polymer Sci 264:77
21. Cosgrove T, Griffiths PC (1994) Colloid Surface A 84:249
22. Pelton RH, Chibante P (1991) Colloids Surf 58:271
23. Stejskal EO, Tanner JE (1965) J Chem Phys 42:288
24. Saarinen TR, Woodward WS (1988) Rev Sci Instrum 59:761
25. Callaghan PT, Le Gros MA, Pinder DN (1983) J Chem Phys 79:6372