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Volume fraction determination of microgel composed of interpenetrating polymer networks of PNIPAM and polyacrylic acid

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Abstract
Interpenetrated polymer network microgels, composed of crosslinked networks of poly(N-isopropylacrylamide) and polyacrylic acid (PAAc), have been investigated through rheological measurements at four different amounts of PAAc. Both PAAc content and crosslinking degree modify particle dimensions, mass and softness, thereby strongly affecting the volume fraction and the system viscosity. Here the volume fraction is derived from the flow curves at low concentrations by fitting the zero-shear viscosity with the Einstein–Batchelor equation which provides a parameter $k$ to shift weight concentration to volume fraction. We find that particles with higher PAAc content and crosslinker are characterized by a greater value of $k$ and therefore by larger volume fractions when compared to softer particles. The packing fractions obtained from rheological measurements are compared with those from static light scattering for two PAAc contents revealing a good agreement. Moreover, the behaviour of the viscosity as a function of packing fraction, at room temperature, has highlighted an Arrhenius dependence for microgels synthesized with low PAAc content and a Vogel–Fulcher–Tamman dependence for the highest investigated PAAc concentration. A comparison with the hard spheres behaviour indicates a steepest increase of the viscosity with decreasing particles softness. Finally, the volume fraction dependence of the viscosity at a fixed PAAc and at two different temperatures, below and above the volume phase transition, shows a quantitative agreement with the structural relaxation time measured through dynamic light scattering indicating that interpenetrated polymer network microgels softness can be tuned with PAAc and temperature and that, depending on particle softness, two different routes are followed.

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Keywords: microgels, volume fraction, viscosity, swelling, softness, PNIPAM

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)
softness. The manuscript is structured as follows: firstly, experimental flow curves for microgels at four PAAc contents and different concentrations are shown and fitted through the cross model to obtain the zero-shear viscosity. Then, the relative zero-shear viscosity is reported as a function of concentration for different samples and compared to the Einstein–Batchelor equation in dilute regime. A factor $k$ to convert the weight concentration in volume fraction is obtained.

The volume fractions derived though viscosity are in good agreement, within the experimental error, with those measured through SLS [39]. Moreover, we report the viscosity behaviour as a function of volume fraction showing that it follows an Arrhenius dependence at low PAAc content and a Vogel–Fulcher–Tammann (VFT) dependence for the highest investigated PAAC concentration. These findings indicate a steepest increase of the viscosity with increasing PAAC content and therefore decreasing particles softness. Finally, an excellent agreement between viscosity and structural relaxation time at two temperatures, respectively below and above the VPT, is found corroborating the idea that softer particles display a dynamical slowing down at higher volume fractions when compared to stiffer ones.

2. Determination of volume fraction from shear viscosity

2.1. Cross equation for the shear rate dependence of viscosity

Microgel suspensions at low concentration display a shear rate ($\dot{\gamma}$) dependent flow behaviour [24, 40] characterized by three different regions: two plateau regions at low and high shear rates ($\eta_h$ and $\eta_\infty$ respectively) and a shear thinning region at intermediate values. The flow curves of microgels can be described through the cross model [41]:

$$\eta = \eta_\infty + \frac{\eta_h - \eta_\infty}{1 + (\frac{\dot{\gamma}}{\dot{\gamma}_c})^m},$$

(1)

where $\eta_0$ and $\eta_\infty$ are the limiting viscosities at zero and infinite shear rate respectively, $\dot{\gamma}_c$ is an intermediate critical shear rate and $m$ is a positive power exponent.

2.2. Einstein–Batchelor equation for the concentration dependence of viscosity in dilute regime

Rheological properties of dilute suspensions depend on the volume fraction $\phi$ (or packing fraction) of the dispersed components [42]. In dilute regime this can be estimated by shear viscosity measurements. Polymer chains, constituting microgel particles, contribute to increase the system viscosity linearly with polymer concentration beyond the viscosity value of the solvent $\eta_s$. At low concentration the virial expansion of viscosity is [43, 44]:

$$\eta = \eta_s(1 + [\eta]C_w + k_H[\eta]^2C_w^2 + \cdots),$$

(2)

where $[\eta]$ is the intrinsic viscosity that for microgels is related to the swelling capability in response to different solvents [43], $k_H$ is the Huggins coefficient representing the viscosity second virial coefficient and $C_w$ the weight concentration. Equation (2) can be rewritten as:

$$\frac{\eta - \eta_s}{\eta_sC_w} = [\eta] + k_H[\eta]^2C_w + \cdots,$$

(3)

where $(\eta - \eta_s)/\eta_s$ is the relative viscosity increment and $(\eta - \eta_s)/\eta_sC_w$ the reduced viscosity. Furthermore, $[\eta]$ can be expressed as the zero-concentration limit of the reduced viscosity:

$$[\eta] = \lim_{C_w \to 0} \frac{\eta_0 - \eta_s}{C_w\eta_s},$$

(4)

where $\eta_0$ is the zero-shear viscosity, $(\eta_0 - \eta_s)/\eta_s$ a dimensionless quantity and the intrinsic viscosity $[\eta]$ is proportional to the reciprocal of the concentration.

For hard spheres the intrinsic viscosity $[\eta]$ is equal to 2.5 [43, 45] and the zero shear viscosity in this case can be written through the Einstein equation:

$$\eta_0 - \eta_s = 2.5\eta_s \phi.$$

(5)

Defining the relative viscosity:

$$\eta_{rel} = \frac{\eta_0}{\eta_s},$$

(6)

equation (5) becomes:

$$\eta_{rel} = 1 + 2.5\phi = 1 + [\eta] \phi.$$

(7)

By replacing equation (5) in (4) the volume fraction occupied by a colloidal particle, expressed in terms of concentration, is:

$$\phi = kC_w,$$

(8)

that allows to connect weight concentration $C_w$ to packing fraction $\phi$. The volume fraction of colloidal suspensions in dilute conditions is estimated from the relative viscosity $\eta_{rel}$ through Einstein–Batchelor equation [46]:

$$\eta_{rel} = 1 + 2.5\phi + 5.9\phi^2$$

(9)

and replacing equation (8) in (9) one gets the relation of the relative viscosity of dilute suspensions as a function of weight concentration $C_w$:

$$\eta_{rel} = 1 + 2.5kC_w + 5.9k^2C_w^2.$$  

(10)

Therefore, fitting the relative viscosity of dilute suspensions as a function of weight concentration $C_w$ through equation (10), the conversion constant $k$ between volume fraction $\phi$ and weight concentration $C_w$ can be obtained.

Nevertheless, the parameter $\phi$ usually defines the volume fraction of hard sphere suspensions and it is expressed as $\phi = nV$, where $n$ is the number density and $V$ the volume of particles. Instead, for soft particles, whose volume is not fixed because of their deformability, the parameter $\zeta$ is introduced. It is generally referred to a generalized volume fraction or sometimes as effective volume fraction and it is defined as:

$$\zeta = nV_0,$$

(11)

where $V_0$ is the volume of an undeformed particle $V_0 = \frac{4}{3}\pi R_0^3$ with $R_0$ the radius measured in dilute conditions. In these
conditions soft particles can be treated as hard spheres and 
$\zeta = \phi$ [1,15]. This assumption is not true out of this regime 
where, at variance with hard spheres, microgel volume can 
change and particles can deform and modify their size as a con-
sequence of the variation of control parameters such as concen-
tration, temperature and pH. For this reason, in this work we 
use the generalized volume fraction $\zeta$ to describe the behaviour 
of soft IPN microgels [1, 15–17] so that equation (8) becomes:

$$\zeta = kC_w$$  \hspace{1cm} (12)

2.3. Arrhenius and VFT models for the concentration 
dependence of viscosity

Outside the dilute regime, a deviation from the Ein-
stein–Batchelor equation is found, in fact the viscosity of co-
loidal suspensions strongly depends on concentration and gen-
erally increases with it. In order to describe this behaviour, 
several models are used but the widespread empirical growth 
is an Arrhenius-like dependence [47, 48] characterized by an 
exponential with two free parameters:

$$\eta = \eta_0 \exp (A\zeta),$$  \hspace{1cm} (13)

where $\eta_0$ is the viscosity value in the limit of $\zeta = 0$ and $A$ 
controls the growth of the function. This dependence marks a 
low sensitivity of viscosity to small changes in concentra-
tion. Instead, if the viscosity is highly sensitive to changes in 
concentration, it is well described by the VFT model [49–51] 
identified by an exponential with three free parameters:

$$\eta = \eta_0 \exp \left( \frac{A\zeta}{\zeta_0 - \zeta} \right),$$  \hspace{1cm} (14)

where $\eta_0$ is the viscosity in the limit of $\zeta = 0$, $A$ is the growth 
parameter and $\zeta_0$ is the critical volume fraction that signs the 
divergence of $\eta$ [14, 50].

This behaviour shares many analogies with molecular 
glasses approaching the glass transition temperature $T_g$ where 
viscosity increases by several orders of magnitude. In fact, 
according to the Angell classification [52], if viscosity is 
slowly sensitive to changes in temperature, it is well described 
by an Arrhenius behaviour and the glass former can be 
classified as ‘strong’ while if it has a much higher tempera-
ture sensitivity, it is well described by a super Arrhenius 
behaviour (VFT or power-law divergence) and the glass is 
defined ‘fragile’.

3. Determination of volume fraction from 
molecular weight

As described in section 2.2, microgel particles are deformable, 
their volume is not fixed and the generalized volume fraction 
$\zeta$ of equation (11) is used, where the number density $n$ can be 
defined as:

$$n = \frac{N_A \rho}{M_w}$$  \hspace{1cm} (15)

with $N_A$ is the Avogadro number, $\rho$ the mass density related 
to the weight concentration of the suspension and $M_w$ the 
molecular weight.

Our aim is to compare the volume fraction obtained from 
viscosity measurements, $\zeta_{\eta}$, with the one obtained from 
the molecular weight, $\zeta_{M_w}$ derived from SLS measurements of a 
previous work [39].

SLS measurements on IPN samples were performed at 
various PAAc contents and concentrations, in dilute regime 
$[5 \times 10^{-6} – 5 \times 10^{-5}]$ g cm$^{-3}$] [39].

The absolute excess scattered intensity $I(Q)$, i.e., the excess 
Rayleigh ratio $R_{ex}$ in cm$^{-1}$, was calculated from the measured 
scattered intensity profile $I_{\text{meas}}(Q)$ as:

$$R_{ex} = \frac{I_{\text{meas}}(Q) - I_{\text{meas}}(0)}{I_{\text{meas}}(0)} \left( \frac{n}{n_{ref}} \right)^2,$$  \hspace{1cm} (16)

where the subscripts ‘solv’ and ‘ref’ refer to the solvent and 
and to the standard reference of toluene. $Q$ is the exchanged wave 
vector, $R_{ex}$ the Rayleigh ratio of the reference at $\lambda = 632.8$ nm, 
n and $n_{ref}$ the refractive index of the sample and of the reference 
respectively.

The excess Rayleigh ratio $R_{ex}$ can be also expressed as the 
product of different terms:

$$R_{ex} = KcM_wP(Q)S(Q),$$  \hspace{1cm} (17)

where $K = \frac{4n^2\pi}{N_Aw} \left( \frac{\Delta n}{n} \right)^2$ is the optical constant, 
c the mass concentration, $M_w$ the molecular weight, $P(Q)$ and $S(Q)$ are 
the normalized form factor and structure factor respectively.

$\Delta n / n$ is the refractive index increment representing the dif-
fERENCE in refractive index between the sample and the solvent 
and was obtained from measurements of IPN dispersions as a 
function of concentration with an Abbe refractometer in a 
range close to that used in SLS experiments. In dilute condition 
(small concentrations $c$) and in the low $Q$ limit, the structure 
factor can be approximated with its value at zero $Q$, $S(0) = (1 + 
2A_2M_wc)^{-1}$, and the form factor with $P(Q) = (1 + Q^2R_g^2/3)^{-1}$ 
where $A_2$ is the second virial coefficient which describes 
the solute–solvent interactions and $R_g$ the gyration radius.

Combining equations (16) and (17) the Zimm equation is 
obtained:

$$\frac{Kc}{R_{ex}} = \frac{1}{M_w} \left[ 1 + \frac{Q^2R_g^2}{3} + O(Q^4) + 2A_2c + O(c^2) \right].$$  \hspace{1cm} (18)

By plotting $Kc/R_{ex}$ as a function of $Q^2 + k^2c$, with $k^2$ a constant 
chosen arbitrarily, one can obtain the Zimm plot from which 
molecular weight, radius of gyration and second Virial coeffi-
cient $A_2$ can be determined. The intercept of a linear interpo-
lation at fixed $Q$, therefore, yields an inverse molecular weight, 
while the slope is proportional to the second virial coefficient. 
Similarly, the radius of gyration is obtained by linear interpo-
lation of the Zimm plot at a fixed concentration. More details 
on the method are reported in a previous paper [39] of some of 
the authors of this.

3.1. Determination of microgel generalized volume fraction $\zeta$ 
at different temperatures

Microgels are characterized by a volume phase transition 
marked by a shrinkage of the particles with a consequent 
change in volume and volume fraction. This determines also
a strong temperature dependence of the \( k \)-values. In order to obtain the volume fraction as a function of temperature, once determined \( \zeta \) at room temperature from viscosity measurements, one can exploit the concept that for isotropic swelling \( \zeta \) can be related to the particle size \( R \) as \([53-55]\):

\[
\zeta(T) = \zeta(T_0) \cdot \left( \frac{R(T)}{R(T_0)} \right)^3
\]

where \( R(T_0) \) is the particle diameter in the reference state and \( R(T) \) is the particle diameter at a given temperature both measured through dynamic light scattering (DLS).

4. Experimental method

4.1. Materials

\( N \)-isopropylacrylamide (NIPAM) monomer (Sigma-Aldrich) and \( N,N' \)-methylene-bis-acrylamide (BIS), (from Eastman Kodak) were recrystallized from hexane and methanol respectively, dried under reduced pressure (0.01 mmHg) at room temperature and stored at 253 K. Acrylic acid (AAc) monomer (Sigma-Aldrich) was purified by distillation (40 mmHg, 337 K) under nitrogen atmosphere in presence of hydroquinone and stored at 253 K. Sodium dodecyl sulphate (SDS), 98% purity, surfactant potassium persulfate (KPS), 98% purity and ammonium persulfate (APS), 98% purity, surfactant potassium persulfate (KPS), hydroquinone and stored at 253 K. Sodium dodecyl sulphate monomer (Sigma-Aldrich) was purified by distillation (40 mmHg, 337 K) under nitrogen atmosphere in presence of hydroquinone and stored at 253 K. Sodium dodecyl sulphate (SDS), 98% purity, surfactant potassium persulfate (KPS), 98% purity and ammonium persulfate (APS), 98% purity, \( N,N',N' \)-tetramethylethylenediamine (TEMED), 99% purity, ethylenediaminetetraacetic acid (EDTA) (a chelating agent for purifying dialysis membranes), and NaHCO\(_3\), (all purchased from Sigma-Aldrich) were used as received. Ultrapure water (resistivity: 18.2 M\( \Omega \) cm\(^{-1} \) at 298 K) was obtained with Sarium\( ^{\text{e}} \) pro ultrapure water purification systems, Sartorius Stedim. All other solvents were RP grade (Carlo Erba) and were used as received. A dialysis tubing cellulose membrane, MWCO 14000 Da, (Sigma-Aldrich) was cleaned before use by washing with running distilled water for 3 h, treated at 343 K for 10 min into a solution containing 3.0% NaHCO\(_3\) and 0.4% EDTA weight concentration, rinsed in distilled water at 343 K for 10 min and finally in fresh distilled water at room temperature for 2 h.

4.2. Microgel synthesis

First PNIPAM) microgels were synthesized by a precipitation polymerization method following the procedure described by Pelton and Chibante \([56]\). Then IPN microgels were obtained interpenetrating PAAc network in PNIPAM microgels by a sequential free radical polymerization method \([29, 36]\). In particular \((24.162 \pm 0.001) \) g of NIPAM monomer, \((0.4480 \pm 0.0001) \) g of BIS and \((3.5190 \pm 0.0001) \) g of SDS surfactant were solubilized in 1560 ml of ultrapure water and transferred into a 2000 ml five-necked jacketed reactor equipped with condenser and mechanical stirrer. The solution, heated at \((343 \pm 1) \) K, was deoxygenated by purging with nitrogen for 1 h. Then the polymerization was initiated by adding \((1.0376 \pm 0.0001) \) g of KPS, dissolved in 20 ml of deoxygenated water and carried out for 4 h. After this time, the resultant PNIPAM microgel was purified by dialysis against distilled water for two weeks changing water frequently. The final weight concentration \( C_w \) of PNIPAM micro-particles was \( C_w = 1.06\% \) as determined by gravimetric measurements. In the second step \((140.08 \pm 0.01) \) g \((C_w = 1.06\%) \) of the recovered PNIPAM dispersion was diluted with ultrapure water up to a volume of 1260 ml into a 2000 ml five-necked jacketed reactor, kept at \((295 \pm 1) \) K by circulating water. Then 5 ml of AAc monomer and \((1.1080 \pm 0.0001) \) g of BIS crosslinker were added to the dispersion and the mixture was deoxygenated by bubbling nitrogen inside for 1 h. 0.56 ml of accelerator TEMED were added and the polymerization was started with \((0.4447 \pm 0.0001) \) g of initiator APS.

IPN microgels with four different PAAc contents were obtained by stopping the polymerization at different reaction times by exposing to air. They were purified by dialysing against distilled water with frequent water changes for two weeks, and then lyophilized and redispersed in water to form a sample at weight concentration \( C_w = 1.0\% \). The PAAc weight concentration \((C_{\text{PAAc}})\) of the four IPN samples were determined by combination of elemental and \( ^1\text{H}-\text{NMR} \) analysis as described in reference \([39]\), and they are \( C_{\text{PAAc}} = 10.6\% \), \( C_{\text{PAAc}} = 19.2\% \), \( C_{\text{PAAc}} = 24.6\% \) and \( C_{\text{PAAc}} = 28.0\% \). Despite the different PAAc content the pKa of microgels should vary slowly as demonstrated in a recent work \([57]\) where the pH-responsive behaviour of PAAc chains with different molar mass was studied. The pKa obtained from the titration data varied in a narrow range around 4.5 is in good agreement with previous works \([58, 59]\). Each PAAc content took almost one month to be synthesized. Samples at weight concentrations \( C_w < 1.0\% \) were obtained by dilution with distilled water from the same stock suspension at \( C_w = 1.0\% \) and adjusted at \( \text{pH} = 5.5 \) while samples at \( C_w > 1.0\% \) were obtained by redispersing a sample lyophilized at \( C_w = 3.0\% \).

4.3. DLS measurements

Particle size of IPN microgels have been determined through DLS measurements using an optical setup based on a solid state laser (100 mW) with monochromatic (\( \lambda = 642 \) nm) and polarized beam. Measurements have been performed at a scattering angle \( \theta = 90^\circ \) corresponding to a scattering vector \( Q = 0.018 \) nm\(^{-1} \) according to the relation \( Q = (4\pi n/\lambda) \sin(\theta/2) \). The average size of the particles has been obtained through the Stokes–Einstein relation \( R = K_B T/6\pi n D_t \) where \( K_B \) is the Boltzmann constant, \( n \) the viscosity and \( D_t \) the translational diffusion coefficient related to the relaxation time \( \tau \) through the relation: \( \tau = 1/(Q^2 D_t) \). The relaxation time \( \tau \) was obtained fitting the autocorrelation function of scattered intensity through the Kohlrausch–Williams–Watts expression, \( g_2(Q, t) = 1 + \beta (\exp[-t/\tau^-\beta])^2 \), with the stretching exponent \( \beta \). Measurements have been performed in dilute conditions at \( T = 298 \) K and \( T = 311 \) K in the swollen and shrunken state respectively and the radii of the microgels are reported in Table 1.
5. Results and discussion

In this section we report the main results of this experimental work. Firstly, in order to determine the volume fraction \( \zeta \) of IPN microgels from viscosity measurements, we performed flow curves at four PAAc contents for different concentrations \( C_w \). In figure 1(a) the viscosity as a function of shear rate \( \gamma \) is reported for IPN microgels at \( C_{PAAc} = 24.6\% \) as an example and the flow curves display a shear thinning behaviour that is more evident at high weight concentrations. Data are fitted through the cross model [equation (1)] that allows to obtain the zero-shear viscosity \( \eta_0 \). In figure 1(b) the comparison among four different PAAc contents, \( C_{PAAc} = 10.6\% \), \( C_{PAAc} = 19.2\% \), \( C_{PAAc} = 24.6\% \) and \( C_{PAAc} = 28.0\% \), at fixed weight concentration \( C_w = 0.3\% \) shows a clear increase of the viscosity with increasing the PAAc content of microgel particles.

Later on, after having obtained the characteristic fit parameters for all flow curves at different \( C_{PAAc} \) and \( C_w \), the normalized shear viscosity \( (\eta - \eta_\infty) / (\eta_0 - \eta_\infty) \) is reported in figure 2 as a function of \( \sigma / \sigma_c \) [24, 25] where \( \sigma \) is the shear stress and \( \sigma_c \) the critical shear stress defined as the stress corresponding to the intermediate shear viscosity \( \eta = (\eta_0 - \eta_\infty) / 2 \). All data for different investigated \( C_{PAAc} \) and \( C_w \) fall into a single mastercurve.

The relative viscosity \( \eta_{rel} = \eta_0 / \eta_\infty \) (6) is plotted in figure 3(a) as a function of weight concentration in dilute regime and a fit through the Einstein–Batchelor expression [equation (10)], letting \( \eta_\infty \) as a free parameter [see SI (https://stacks.iop.org/JPCM/33/174004/mmedia)], provides the conversion factor \( k \) [equation (12)] that directly links the polymer concentration \( C_w \) to the volume fraction \( \zeta \). Moreover, figure 3(a) shows a strong \( C_{PAAc} \) dependence of the relative
Figure 2. Scaled plot of $\frac{(\eta - \eta_\infty)}{(\eta_0 - \eta_\infty)}$ against reduced shear stress for IPN microgels at four PAAc contents ($C_{\text{PAAc}} = 10.6\%$, $C_{\text{PAAc}} = 19.2\%$, $C_{\text{PAAc}} = 28.0\%$ and $C_{\text{PAAc}} = 24.6\%$), at different weight concentrations and at $T = 298$ K. All data follow a unique mastercurve.

Figure 3. (a) Relative viscosity from equation (6) as a function of weight concentration at $T = 298$ K. Data are fitted according to Einstein–Batchelor model of equation (9). (b) Volume fraction $\zeta$ versus weight concentration. The angular coefficient of the linear fit represents the conversion constant $k$ between weight concentration $C_w$ and volume fraction $\zeta$ as reported in equation (12).

Viscosity with a more pronounced growth for the samples at $C_{\text{PAAc}} = 24.6\%$ and $C_{\text{PAAc}} = 28.0\%$ confirming that the viscosity is highly influenced by PAAc and weight concentration. The volume fraction $\zeta$ as a function of concentration $C_w$ is shown in figure 3(b) for the four PAAc contents investigated and the $k$ parameter is the slope of the curves. Values of the $k$ parameter are reported in table 1 for each $C_{\text{PAAc}}$ at room temperature, showing that $k$ becomes greater with increasing
Figure 4. Volume fraction versus weight concentration for IPN microgels with \( C_{\text{PAAc}} = 10.6\% \) and \( C_{\text{PAAc}} = 19.2\% \), at \( T = 298 \) K, as obtained by rheology (full symbols) and SLS measurements (open symbols). Lines are linear fit to the data. (b) Volume fraction obtained through SLS from the molecular weight, \( \zeta_{M_w} \) as a function of the volume fraction found by rheology, \( \zeta_{\eta} \). The straight line has slope 1.

with the one found from the molecular weight, \( \zeta_{M_w} \). In order to better visualize the comparison between the two methods, \( \zeta_{M_w} \) is plotted versus \( \zeta_{\eta} \) in figure 4(b) and we can confirm that, within the experimental error, the curves are close to that with slope 1, corresponding to perfect agreement.

The normalized viscosity behaviour at all the investigated concentrations, in addition to those in the dilute regime, is reported in figure 5 at different PAAc (and crosslinker) contents. To avoid misunderstandings, we define the viscosity at zero shear rate \( \eta_0 \) obtained from the Cross model as \( \eta_0 \). While \( \eta_0 \) represents the viscosity in the limit of zero volume fraction from equations (13) and (14). It can be seen that the growth of the viscosity is more gradual for lower PAAc (and crosslinker) contents and it is well fitted with an Arrhenius dependence [equation (13)]. In contrast, at the highest investigated PAAc (28.0\%) where a VFT dependence [equation (14)] well reproduces the data, its divergence moves to lower volume fractions and its increase is much more steep. Data are also compared with the behaviour of hard spheres viscosity plotted as a dash-dot line according to equation (14) with \( A = 1 \) and \( \zeta_0 = 0.58 \). These outcomes also evidence that, with decreasing particles softness, the viscosity divergence occurs at lower \( \zeta \) up to the limiting value of hard spheres, \( \zeta_0 = 0.58 \), demonstrating how the peculiarity of microgels to swell, deform and interpenetrate allows \( \zeta \) to reach, at high concentrations, values above 1 for softer particles.
Figure 5. Normalized shear viscosity as a function of volume fraction $\zeta$ at $T = 298$ K. Lines represent fits through Arrhenius model [equation (13)] for IPN microgels with $C_{PAAc} = 10.6\%$, $C_{PAAc} = 19.2\%$ and $C_{PAAc} = 24.6\%$, VFT model [equation (14)] for IPN microgel with $C_{PAAc} = 28.0\%$ and VFT for hard sphere with $A = 1$ and $\zeta_0 = 0.58$ (dash-dot line).

Figure 6. Normalized shear viscosity (closed symbols) and relaxation time (open symbols) vs volume fraction below ($T = 298$ K) and above ($T = 311$ K) the VPT for IPN microgel with $C_{PAAc} = 24.6\%$. Lines represent fits according to the Arrhenius expression [equation (13)] for $T = 298$ K and to the VFT expression [equation (14)] for $T = 311$ K.
These findings are in good agreement with the behaviour of the normalized structural relaxation time $\tau_0/\tau$ reported in a previous work [35] for IPN microgels with different PAAc contents and at a temperature, $T = 311$ K, above the VPT. Here $\tau_0/\tau$ increases more rapidly at higher PAAc contents, with increasing weight concentration following always a VFT behaviour [equation (14)]. Accordingly, a direct comparison between normalized structural relaxation time and viscosity for an IPN microgel at $C_{\text{PAAc}} = 24.6\%$ is reported in figure 6 at two temperatures, $T = 298$ K and $T = 311$ K, below and above the VPT in the swollen and shrunken state respectively. In order to calculate the volume fraction at $T = 311$ K, viscosity measurements as a function of concentration in dilute regime were performed and the conversion factor $k$ between weight concentration and volume fraction was found through the Batchelor model as performed at room temperature ($T = 298$ K). Moreover exploiting the concept that for isotropic swelling, $\zeta$ can be related to the particle size $R$ through equation (19), the comparison between the volume fraction measured at $T = 298$ K and that calculated at $T = 311$ K is reported in SI. We found that structural relaxation time and viscosity are in excellent agreement, both growing gradually and being well described by an Arrhenius dependence at $T = 298$ K below the VPT while they increase more steeply with at $T = 311$ K above the VPT following a VFT behaviour [equation (14)]. Also in this case, two different models are used below and above the VPT since the microgel softness increases with decreasing temperature across the VPT. Therefore, it is clear that the volume fraction dependence of viscosity and relaxation time is well described by an Arrhenius law for softer particles as in the case of low PAAc (and crosslinker) at temperatures below the VPT (figures 5 and 6). On the contrary, they follow a VFT law for less soft particles at high PAAc ($C_{\text{PAAc}} = 28.0\%$) and crosslinker content (figure 5) or at temperatures above the VPT (figure 6), validating the idea that softness can be controlled by PAAc, crosslinker and temperature.

6. Conclusions

In this work we have determined the volume fraction of an IPN microgel composed of PNIPAM and PAAc through viscosity measurements at different PAAc contents and weight concentrations. Experimental flow curves have been fitted through the cross model that allows to gain information on the zero-shear viscosity. This is used both to plot a mastercurve of viscosity data and to determine, through the Einstein–Batchelor equation, the shift factor $k$ to convert the weight concentration to volume fraction. Moreover viscosity behaviour as a function of $\zeta$ has highlighted an Arrhenius-like and a VFT dependence for microgels with low and high PAAc content respectively. Interestingly a comparison with hard spheres indicates a steepest increase of the viscosity with decreasing particles softness. A similar scenario is found below and above the VPT, in good agreement with the structural relaxation time behaviour, indicating that softness in IPN microgels can be tuned with PAAc, crosslinker and temperature and that, depending on particle softness, two different routes are followed.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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