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The effect of surface modification on the stability characteristics of poly(*N*-isopropylacrylamide) latices under Brownian and flow conditions

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Abstract: The stability of thermoreversible microgel particles of poly(N-isopropylacrylamide) having carboxylate surface charge groups has been studied in the presence of electrolyte and non-adsorbing polymer. Methylation of the surface charge groups leads to a decrease in the electrophoretic mobility of the particles and also the interparticle electrostatic repulsive potential, resulting in the material becoming more susceptible to flocculation. The Hamaker constant of the microgel particles increases with the decrease in the hydrodynamic size of the particles following heating. This brings about an increase in the van der Waals attractive energy which results in the particles aggregating in the presence of sufficient electrolyte. Under conditions of flow through membranes, where shearing forces are operative, the flocculation observed following the heating of the dispersions results in the blockage of pores.

Key words: Microgel – poly(N-isopropyl-acrylamide) – surface methylation – stability – aggregation

Introduction

In a previous publication [1] the temperature-controlled, reversible flocculation of poly(N-isopropylacrylamide) particles on the addition of electrolyte on non-adsorbing polymer was described. The particles studied were prepared by an emulsion polymerisation method developed by Pelton and Chibante [2] using a persulphate initiator in water at 70 °C. At 25 °C the dispersion was stable at a result of solvated polymer chains extending away from the particle surface leading to a steric barrier, preventing flocculation. Further, as the particles are swollen with water at this temperature, their Hamaker constant is close to that of the solvent. Hence, the van der Waals attractive force between the particles is negligibly small. At 40 °C, however, the particles shrink to become effectively hard spheres as a result of an increase in the Flory [3] interaction parameter (χ) for the poly(NIPAM)/water system. This facilitates more polymer-polymer contacts. Hence the particles contract, forcing out solvent from the interstitial spaces. Aggregation of the dispersion can now take place in the presence of sufficient electrolyte (which leads to the screening of the electrical double layer repulsion between the particles), as a result of the increase in the van der Waals attractive forces. Further, in the presence of non-adsorbing poly(styrene sulphonate), flocculation of the particles takes place as a result of depletion forces [4, 5] between the particles. On cooling the flocculated dispersions from 40 ° to 25 °C the particles redisperse as a result of reswelling. This process of flocculation and subsequent redispersion can be repeated many times by heating and cooling the particles.

In this paper the preparation of poly(N-isopropylacrylamide) latices using a carboxy initiator, followed by the subsequent methylation of a portion of the resulting latex, is described. Methylation was carried out in an attempt to

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reduce the number of charged groups on the particle surface and make it less hydrophilic. A series of experiments comparing the stability characteristics of the original and methylated particles, as a function of temperature, electrolyte and polymer concentration, are outlined. It is well known that shearing forces cause flocculated networks of colloidal particles to break up and a number of attempts has been made to model this process [6, 7] in terms of the deformation of the macrostructure of the flocculated material. The stability characteristics of the particles under conditions of flow are therefore also considered in an attempt to determine what effect modifying the surface of the particles may have on the resistance of the dispersions to break up under the prevailing shearing forces.

Experimental

Materials

Poly(N-isopropylacrylamide) latex was prepared by dissolving 0.5 g of 4.4/-azobis(4-cyanopentanoic acid) (Fluka Chemicals) in 900 cm^3 of distilled water at pH 9. The solution was placed in a three-necked, round-bottom flask, immersed in an oil bath at 70 °C, fitted with a stirrer, having nitrogen gas entering at one neck and a water-cooled condenser at the other. A further 100 cm^3 of aqueous solution containing 2.5 g of dissolved *N*-isopropylacrylamide (Kodak Ltd) and 0.5 g methylene bisacrylamide (BDH Chemicals Ltd) was added to the solution under high agitation. After 30 min the solution became turbid; the reaction was then left for 6 hours, resulting in a milky white dispersion. The latex was allowed to cool and then filtered through glass wool before being extensively dialysed against distilled water, changing the dialysate twice daily for 1 week. Dry weight analysis of the latex showed the sample to be 0.33% w/w, a yield of 95%.

Methylation of the carboxyl surface groups was achieved by placing 250 cm^3 of the latex in a breaker with 25 cm^3 of dimethyl sulphate (Koch Light Labs. Ltd.), in large molar excess, and stirring at 30 °C overnight. The resulting dispersion was then extensively dialysed against distilled water to remove any unreacted material.

Transmission electron micrographs showed both the original and methylated latices to consist of monodispersed spheres having a mean diameter of 240 nm $\pm$ 12 nm. Poly(styrene sulphonate) Mw 95 600 (Mw/Mn 1.1) was purchased from Polymer Laboratories Ltd, Shropshire.

Characterisation of microgel particles

Electrophoretic mobility measurements were carried out on both latex samples, in aqueous NaCl solutions using a Pen Kem "System 3000" electrophoresis apparatus.

A potentiometric titration was performed on each microgel dispersion using a Ciba-Corning "Checkmate" conductivity meter. 25 cm^3 of each dispersion was placed in a clean beaker and titrated with 0.01 mol dm^{-3} HCl, whilst been stirred continuously. The procedure was repeated to ensure reproducibility.

The temperature dependency over the range 25 ° to 50 °C of the particle radius of the two poly(NIPAM) latices was determined by photon correlation spectroscopy using a Malvern Instrument type "7027" dual LOGLIN correlator, equipped with a krypton-ion laser ($\lambda = 530.9$ nm). The scattering angle was fixed at 90 °.

Stability experiments

The "static" stability experiments were carried out using dispersions of 0.1% (wt/vol) microgel particles, containing various concentrations of sodium chloride. The samples were placed in a water bath at 25 ° or 40 °C and allowed to stand overnight. The extent of any aggregation in the dispersion was estimated from the wavelength dependence of the turbidity of the dispersions [8]; $n = [d(\log \text{turbidity})/(d(\log \text{wavelength})]$. Similar experiments were carried out at both temperatures using poly(styrene sulphonate) in place of NaCl.

The flow experiments were carried out using the apparatus illustrated schematically in Fig. 1A 0.1% dispersion of the carboxylated latex containing 0.5 mol dm^{-3} NaCl was pumped at a flow rate of 10 cm^3 per hour through a "Nucleopore" membrane having a pore diameter of 3 μm, After 2 cm^3 of eluent had passed through the membrane, and ensuring that the pressure transducer attached across it recorded a "zero" reading, the

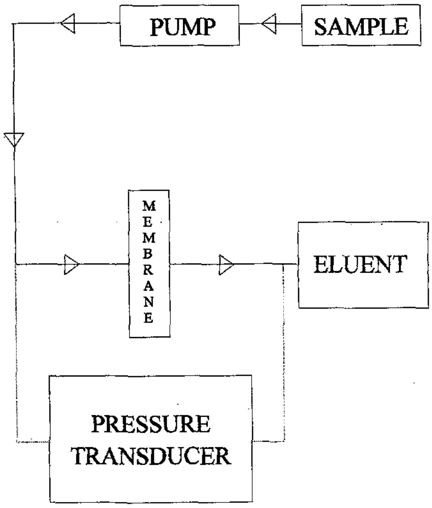

Fig. 1. A schematic representation of the flow pressure apparatus

membrane was inserted into a water bath at 40 °C. This was removed once any increase in pressure difference across the membrane was noted. The experiment was repeated using the methylated latex, and then for both samples using a membrane having a 5 μm pore diameter. The experiment was also carried out in the presence of poly(styrene sulphonate) in place of NaCl.

Results

Characterisation of microgel particles

Variation of the hydrodynamic diameter of the carboxylated poly(NIPAM) particles, as a function of temperature, is illustrated in Fig. 2. It can clearly be seen that the particles shrink from 265 ± 3 nm at 25 °C to 130 ± 3 nm at 50 °C corresponding to an eight-fold reduction in particle volume. Re-cooling the dispersion to 25 °C resulted in the particles adopting their original size with no hysteristis taking place between the heating and cooling cycle. This process could be carried out many times with no adverse effect on the particles. Methylation of the dispersion had no effect on the swelling and shrinking behaviour, the temperature dependence of the particle diameters begin the same for both materials.

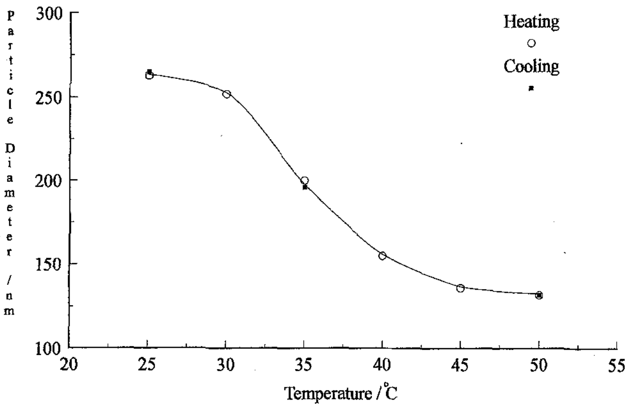

Fig. 2. Particle diameter versus temperature for a 0.01% dispersion of poly(N-isopropylacrylamide) particles

Table 1. Electrophoretic mobility (μ) of microgel particles in 10^{-3} M NaCl as a function of temperature.

T/°C	Carboxylated $\mu \times 10^8/m^2s^{-1}V^{-1}$	Methylated $\mu \times 10^8/m^2s^{-1}V^{-1}$	Radius a/nm
25	− 1.0	− 0.7	132
30	− 1.4	− 1.2	126
35	− 1.9	− 1.6	100
40	− 2.5	− 2.1	78

Table 1 shows how the electrophoretic mobility of the carboxylated and methylated particles varies with temperature in a background electrolyte of 10^{-3} mol dm^{-3} NaCl.

Two trends which emerge from these data are firstly that the mobility increases with temperature. Secondly the mobility, at a fixed temperature, is lower, as expressed for they methylated particles. However, the mobility is not zero, indicating that only partial methylation of the surface caboxylic acid groups has occurred under the conditions used in the methylation reaction. This result is confirmed by the potentiometric titration results, at 25 °C, which indicate that the number of charged groups per particle decreases from 485 for the carboxylated latex to 230 for the partially methylated particles.

Figure 3 illustrates how the stability of both the carboxylated and partially methylated microgel particles varies as a function of temperature, at a fixed background electrolyte concentration on 5×10^{-2} mol dm^{-3} NaCl solution. The critical flocculation temperature (CFT) is at 43 °C for the carboxylated sample and 36 °C for the partially methylated particles.

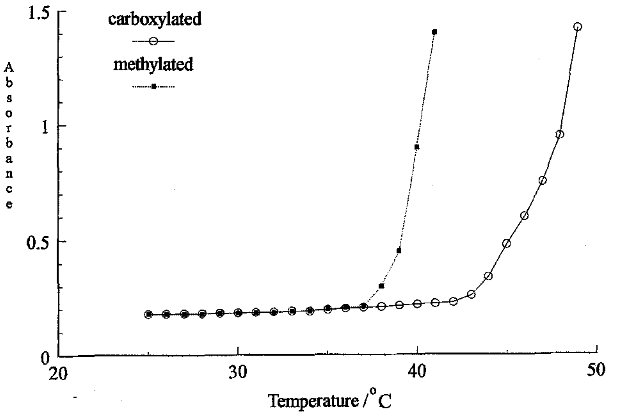

Fig. 3. Absorbance at 547 nm versus temperature, for 1% dispersions of the carboxylated and partially methylated poly(N-isopropylacrylamide) microgel latices in 5×10^{-2} mol dm^{-3} NaCl

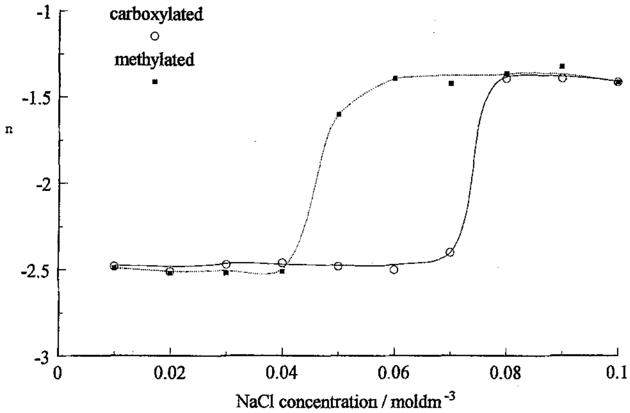

Fig. 4. n versus sodium chloride concentration for 1% dispersions of the carboxylated and partially methylated poly(N-isopropylacrylamide) microgel latices at 40 °C

Figure 4 shows that, at a fixed temperature (40 °C), the carboxylated latex aggregates at NaCl concentrations in excess of 0.06 mol dm^{-3}, whilst the methylated sample aggregates at NaCl concentrations of the order of 0.04 mol dm^{-3} and above. Both figures show that even partial methylation of the latex particles reduces their stability in the presence of electrolytes.

In Fig. 5, the effect of addition of (non-adsorbing) poly(styrene sulphonate) on the stability of both dispersions is illustrated. The critical flocculation concentration (CFC) of the carboxylated latex is at 0.7% (w/v) polymr while the CFC of the methylated latex is 0.6% (w/v) polymer.

Figure 6 shows how the differential pressure across a membrane having a pore size of 3 μm varies with elution volume for both samples of poly(NIPAM) in the presence of 0.5 mol dm^{-3} NaCl. Following the immersion of the membrane holder in a water bath at 45 °C (point A), aggregation occurs rapidly resulting in an increase in the differential pressure across the membrane. At point B blocking took place. At this point the eluent was clear and free from any microgel particles. On reducing the temperature, following the removal of the membrane holder from the water bath at point B, the pressure quickly returned to zero. The eluent became turbid indicating the particles had redispersed and were once again passing through the pores of the membrane. No significant difference was observed in the behaviour of either microgel, though the partially methylated sample was slightly more efficient at blocking the membrane than its carboxylated counterpart.

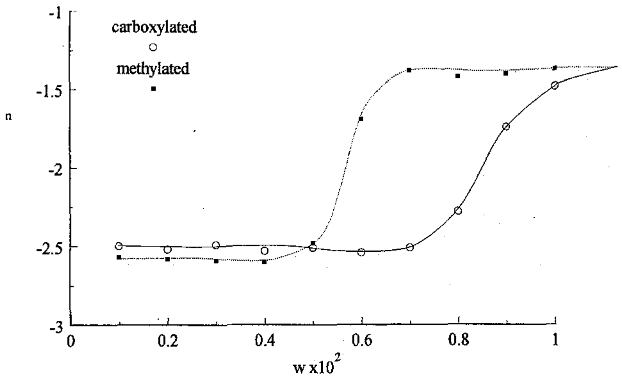

Fig. 5. n versus polymer w/v fraction (w) for 1% dispersions of the carboxylated and partially methylated poly(N-isopropylacrylamide) microgel latices at 40 °C

The experiment was repeated using a 5 μm pore diameter membrane, and the results are shown in Fig. 7. Following the immersion of the membrane into the water bath at point A, no increase in pressure occurred with the methylated sample of poly(NIPAM) until point B. With the carboxylated microgel no pressure increase occurred until point B′. This clearly illustrates that the larger pore diameter membrane requires larger flocs to form before blocking occurs. The membrane was removed from the water bath at point C and C′, respectively, for the carboxylated

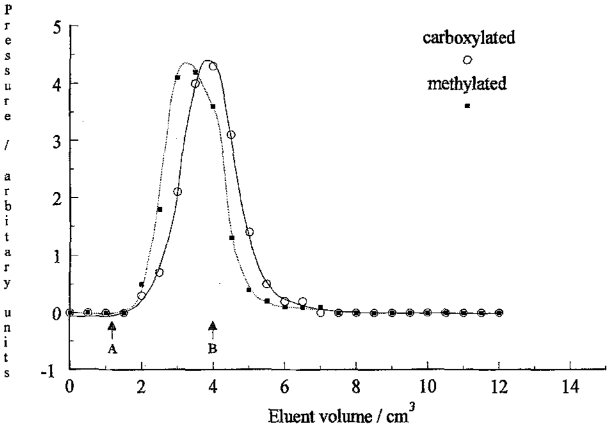

Fig. 6. Differential pressure versus eluent volume for a carboxylated and partially methylated poly(N-isopropylacrylamide) microgel particles in 0.5 mol dm^{-3} NaCl, using a 3 μm membrane at 45 °C

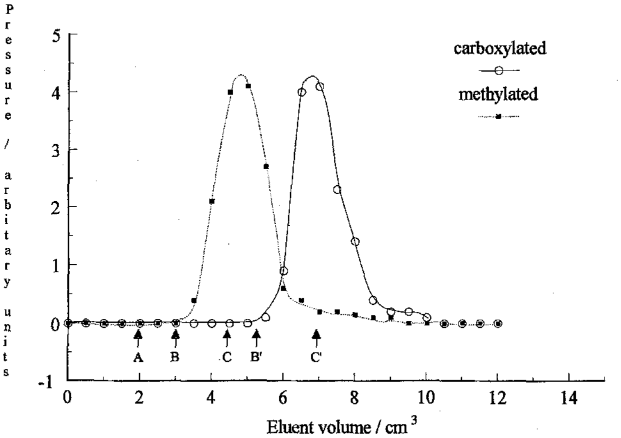

Fig. 7. Differential pressure versus eluent volume for a carboxylated and partially methylated poly(N-isopropylacrylamide) microgel particles in 0.5 mol dm^{-3} NaCl, using a 5 μm membrane at 45 °C

and partially methylated latex samples. In both cases the pressure began to decrease slowly. However, the methylated sample took slightly longer to fully redisperse to the point where particles were freely passing through the membrane and for the pressure to return to zero.

Repeating the above flow experiment using the poly(NIPAM) microgels in the presence of 1% (w/v) poly(styrene sulphonate) solution did not result in any significant blocking of the membrane or any increase in pressure for the carboxylated sample. However, with the methylated microgel, blocking took place at a total elution volume of 5.5 cm^3. This was a significantly larger elution volume for blocking to occur than was required with 0.5 mol dm^{-3} NaCl.

Discussion

The fact that flocculation of that microgel particles only occurs on heating can be accounted for semi-quantitatively by estimating the van der Waals attraction energy (V_A), as a function of particle separation (h), at differing temperatures. An approximate form for V_A is given by,

$$V_A = -\frac{\left(A_M^{1/2} - A_W^{1/2}\right)^2 a}{12h}, \tag{1}$$

where A_M is the Hamaker constant of the microgel particle, A_W that of the medium (water and a particle radius. A_M will be a function of temperature. For composite particles, such as swollen microgel particles, Vincent [9] has derived the following relationship for the Hamaker constant,

$$A_M = \left[A_P^{1/2}\phi + (1-\phi)A_W^{1/2}\right]^2, \tag{2}$$

where A_P is the Hamaker constant of the polymer, and ϕ is the (mean) volume fraction of the polymer in the swollen latex particles. ϕ is given by,

$$\phi = \left(\frac{a_h}{a_T}\right)^3, \tag{3}$$

where a_h is the radius of the contracted (hard-sphere) particles and a_T that of the swollen particle at temperature T.

Figure 8 shows $V_A(h)$ curves for the microgel particles (either type) at different temperatures. In this case, a_h was taken for the value at 40 °C (Table 1). The value for A_P and A_W were taken to be 6.6×10^{-20} J (assuming the value for polystyrene since the value of poly(NIPAM) is not known) and 3.7×10^{-20} J [10], respectively.

It may be seen that the van der Waals attraction increases significantly with temperature, as expected. Assuming, somewhat arbitrarily, that the "contact" separation of two latex particles is ~ 0.2 nm, then the contact energy is ~ 1.6 kT at

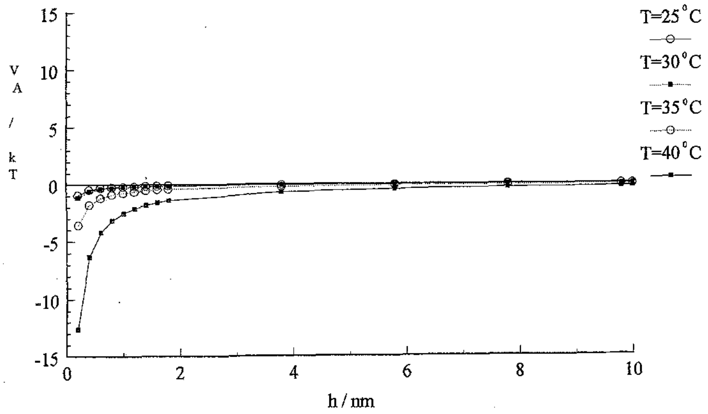

Fig. 8. Theoretical plot of the van der Waals attractive energy (V_A) versus particle separation (h) for poly(N-isopropylacrylamide) microgel particles in water as a function of temperature

25 °C, increasing to ~ 10 kT at 40 °C. At 25 °C, therefore, thermal energy should be sufficient to keep the microgel latex stable, even in the absence of the electrostatic repulsion forces, arising from the charged groups at the surface of the particles.

It is difficult to estimate in any precise way the electrostatic interaction between the microgel particles. Firstly, it is difficult to obtain the surface, or zeta potential of the particles, i.e. the potential at the boundary between the (swollen) particles and the continuous phase. Equations relating the mobility and the zeta potential for *hard* spheres, such as that given by O'Brien and White [11], are not valid for *soft* particles, such as microgels. Oshima et al. [12, 13] have considered the case of particles carrying a polyelectrolyte shell, which would also be applicable to microgel particles. They give the following expression for the mobility, u:

$$u = \frac{\varepsilon_r \varepsilon_0}{\eta} \left[\frac{\psi_0/\kappa_m + \psi_{DON}/\lambda}{1/\kappa_m + 1/\lambda} \right] + \frac{zeN}{\eta \lambda^2} , \tag{4}$$

where ψ_0 is the surface potential and ψ_{DON} the Donnan potential in the polyelectrolyte layer, $\lambda = (v/3)^{1/2}$ where v is the frictional coefficient of the polyelectrolyte layer and η is the viscosity of the bulk solution; N is the number density of charged groups (valency z) in the polyelectrolyte layer. κ and κ_m are the Debye-Hückel parameters for the bulk solution and the polyelectrolyte layer, respectively. Application of Eq. (4) requires many parameters which are difficult to assess, in particular v and N. N is assumed to be *uniform* throughout the shell (or microgel particle). This is a gross assumption; one expects N to decrease monotonically from the inside to the periphery of the polyelctrolyte shell. In view of this, no attempt was made here to calculate ψ_0 as a function of temperature or electrolyte concentration, although further consideration of this point will be given in a subsequent paper.

A further difficulty is that we really need to estimate the surface (or zeta) potential of the particles, at electrolyte concentrations at, and close to, coagulation conditions. However, by way of illustration, some total interaction energy (electrostatic plus van der Waals) plots, as a function of temperature, at fixed electrolyte concentration (5×10^{-2} mol dm^{-3} NaCl), for the carboxylated microgel particles, are shown in Fig. 9.

The electrostatic energy, $V_E(h)$, was calculated using [9]:

$$V_E = 2\pi\varepsilon\varepsilon_0 a \zeta^2 \exp(-\kappa h) , \tag{5}$$

where ε and ε_0 are the permittivity of the medium and free space, respectively, and κ is the reciprocal thickness of the electrical double layer [14]. Somewhat arbitarily, a value of -10 mV was chosen for the zeta potential of the carboxylated particles at 5×10^{-2} mol dm^{-3} NaCl, *independent* of the temperature. This is a "guess" based on extrapolation of values given at lower electrolyte concentrations for "hairy" polystyrene latex particles in earlier work [15]. Despite all the assumptions involved, the trends with temperature for the $V(h)$ curves, shown in Fig. 9, do support the ex-

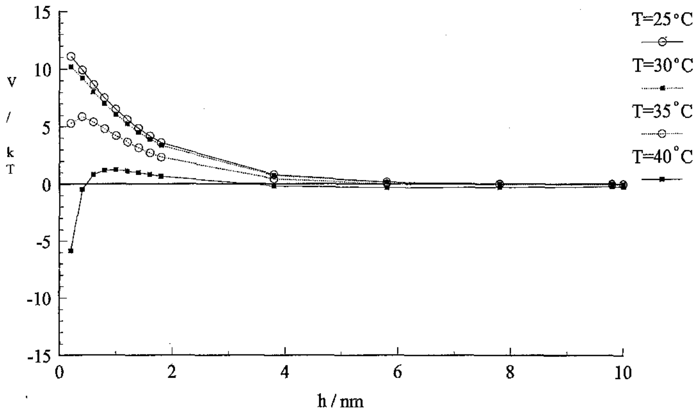

Fig. 9. A plot of the total potential energy (*V*) versus separation (*h*) for a poly(N-isopropylacrylamide) microgel particle in water as a function of temperature

perimental data shown in Fig 3, which shows how the stability of the microgel dispersions depends on temperature. The experimental CFT values were found to be 43° and 36 °C for the carboxylated and partially methylated microgel dispersions, respectively. Figure 9 shows that around 40 °C for the carboxylated microgel particles the maximum in the *V*(*h*) plot is reduced to ~ 2 kT, i.e., sufficiently low for thermal energy (Brownian motion) to cause flocculation.

In the presence of poly(styrene sulphonate) at 40 °C the particles flocculate as a result of depletion forces operative in the system. It is unlikely that the polymer will adsorb onto the particles from water as both species have negative charges. Depletion flocculation occurs more readily with the methylated particles as the repulsive potential is significantly lower for the methylated particles than for the carboxylated microgel. Hence a less strong depletion interaction is required to induce flocculation. The destabilised latex redispersed on cooling to 25 °C. The very soft particle surface at this temperature would require a very high polymer concentration to flocculate the dispersions. Clarke and Vincent [16], who studied the stability of non-aqueous polystyrene microgel dispersions, in the presence of free polystyrene polymer, reported the CFC of the polymer increased significantly as the microgel became more swollen and softer. Furthermore, in a recent publication, Milling et al. [17], who studied the effect of grafted chain coverage on the depletion flocculation of sterically-stabilised silica particles, demonstrated that the CFC of added polystyrene also increased initially with increasing surface coverage of grafted polymer (i.e. softness of the particle), up to some limiting value.

Under conditions of flow particles experience shearing forces which can break up the macrostructure of any flocculated network. In the case of the microgel particles modification of the surface of the particle by methylating at least a fraction of the carboxylic acid groups appears to increase the cohesion of the floc, as expected. The results are consistent with the "static" stability experiments which suggest that the methylated particles flocculate more readily and, therefore, probably form more extensive flocculated networks.

The reason why the carboxyl microgels have a greater resistance to blocking the membrane in the presence of free polymer compared too the partially methylated, has to do with the fact that the polymer concentration used (1%) was only just above the CFC for the carboxylated microgel (Fig. 6) and under dynamic conditions the depletion attraction may be weaker. This is clearly an area for further investigation.

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