Residual temperature dependence of normalized diffusion of polystyrene latex in aqueous solvents

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The so-called anomalous dependence of diffusion of polystyrene latex[4] was examined in detail using quasi-elastic light scattering. The normalized diffusion coefficients showed a residual decrease with increasing temperature for solutions in water, 0.1 M phosphate buffers, methanol and 0.1 M sodium carbonate but not in dilute solutions of dimethyl ketone, Triton X-100, some salt solutions and pure ethanol. Using sensitive analyses for multi-exponential fits to the data, it was shown that the presence or absence of the dependence was not affected by possible low levels of aggregation of the latex. These results are interpreted as reflecting an increased solvation of the charge groups on the latex with rising temperature.

INTRODUCTION

The interactions of solvents with polymers is usually measured through virial coefficients. Changes in these with rising or falling temperatures can be described through the influence that temperature has on the interaction. Unfortunately there are many changes that can occur with rising temperature and some of these are not usually included within the meaning of virial coefficients. Among these is oligomerization to produce changed amounts of aggregates at various temperatures, while another is changing patterns of solvation. We have been examining the early stages of these processes using diffusion methods and in this paper we examine the limits in the measurements using polystyrene latex as the experimental material.

The diffusion of a polymer in a solvent is a relatively sensitive estimate of its solvated radius, and since the advent of photon correlation spectroscopy the diffusion coefficients of moderately sized particles can be reproducibly measured. Thus, with this technique it is possible to explore the influence that temperature has on the activities of these polymers in good and bad solvents. Several reports[1-4] show that there remains a residual decrease in diffusion coefficients even after the measured coefficients had been normalized to a standard temperature using the Einstein–Stokes relationship. Since there is no question that this relationship is a true model for diffusion of polymers, it is tempting to relate the changes to increased thermal motion of the intrinsic chains of the polymer. However, the question of whether dimerization or changed solvation is occurring clouds the argument. Classical light scattering studies of polystyrene in cyclo-

hexane show comparatively large increases in the average radius of gyration with increasing temperature[5]. Relatively high concentrations of the polymer were necessary for this work and the second virial coefficient contributed a significant effect to the calculations. Thus, it is not possible to use these measurements for interpretation of molecular activities without knowing whether increased amounts of aggregates were present at raised temperatures. In other words there are several explanations for the effect that temperature has on solvated latex particles. Possibly the most important as far as the diffusion measurements are concerned are: (1) the change in value for the virial coefficients caused by increased temperature[5] which leads to small decreases in $D(20, w)$; (2) a change in the equivalent hydrodynamic coefficients used to describe the concentration dependence of the frictional coefficient; (3) an increase in the solvation of the polymer, so increasing the effective radius of the polymer without any significant influence on the interchain activities; (4) interparticle aggregation. These effects are all correlated to greater or lesser extents, but by changing the experimental conditions it is possible to separate some of the effects. With polystyrene latex it is possible to obtain relatively accurate estimates of diffusion coefficients at concentrations where factors (1) and (2) can be ignored (around 10^{-6} g cm^{-3}). Thus it remains to be seen whether effects caused by (3) and (4) can be separated by making measurements at low concentrations and analysing the decay curves by two independent methods.

EXPERIMENTAL

Two independent samples of polystyrene latex were

purchased from Polaron (UK) (these are reputed to be Dow latex) and the nominal diameter of both samples was 109 nm, which corresponded with that calculated from the measured diffusion coefficients made at 288K in water. Aliquots from these suspensions were diluted in the appropriate solvents to produce concentrations of between 1 μg cm^{-3} and 4 μg cm^{-3}; these concentrations are based on dry weight estimates of the concentrations of the original suspensions. These samples were injected into cuvettes through a 220 nm Millipore filter and examined immediately. Storing the diluted samples at room temperature and remeasuring at intervals over a period of several weeks showed that the diffusion coefficients measured at 293K remained constant within the experimental errors. Other reagents such as buffer salts were analytical grade and made up in glass distilled water.

Diffusion coefficients (D) were measured using standard photon correlation spectroscopy as described previously[4]. The 'clipped' counts were autocorrelated using a Malvern correlator (Malvern Instruments Ltd, Malvern, UK) having 48 channels. We were concerned to show that the effects we observed were not artifacts caused by malfunctioning of our equipment so we compared results obtained in Birmingham with those measured at Malvern Instruments Ltd for the same samples. This second instrument was a K7027 correlator with 64 channels, and a 25 mW helium–neon laser as a light source.

The results of measurements of scattered light are relaxation curves which, for a monodisperse particle having dimensions less than the wavelength of the light, follow the exponential relationship:

$$g^{(2)}(\tau) = 1 + \exp(-\lambda\tau). \tag{1}$$

Here $g^{(2)}(\tau)$ is the second-order correlation function collected at time τ while $\lambda = DK^2$ (K is the scattered wave vector). In the present work we employed time intervals (τ) of 20 μs for the accumulation of functions. For polydisperse components the right-hand side of equation (1) must be expanded to include a sum of exponentials. Thus, in the interpretation of the relaxation curve it is necessary to test for multicomponent relaxation; if the test is positive then attempts must be made to separate the coefficients. In the present work this analysis was made using the procedure described by Provencher[6] in which the data were first smoothed using a weighted function and then fitted to a series of exponentials using a Laplacian transform. Internal statistical tests assign probabilities of significance to the numbers of components. These procedures provide z-average estimates of the diffusion coefficients of the components. Provencher has incorporated the procedure into a program called DESCRETE which he kindly supplied to us. This has been used to analyse the data from polystyrene latex. The data from Malvern Instruments Ltd were analysed for polydispersity by the additional procedure of cumulants[7,8] as well as DESCRETE.

Experiences accumulated from measuring many solutions of polystyrene latex have shown that reproducibility of the absolute diffusion coefficients is about ±6% while that for one experiment is about ±0.5%. At every temperature a minimum of three accumulations were measured and analysed.

Both washed plastic and glass cuvettes (1 cm path length) of square cross section were employed in the work but no significant differences were found between the two types. They were inserted in the light scattering cell and their temperatures maintained by immersion of the cuvette in water controlled through a sensor inserted in the cell. The temperature in the cuvettes was recorded during the experiments and once equilibrium had been achieved (taking about 5 min for each 5K increment) the value was constant to ±0.1°C over the range examined. The light source was a Spectra Physics argon ion laser Model 171 operating in the single mode at a wavelength of 488 nm, and minimum power (less than 50 mW) was used for all measurements.

The densities and viscosities of solvents were taken from tables in *The Handbook of Chemistry and Physics*, vol. 53 (CRC).

RESULTS

The initial experiments confirmed the changes reported earlier[4] but, since estimates made by Provencher's procedure include more objective estimates of baselines than the previous procedures, the present results are more reliable. Many separate measurements were made using both samples of latex and when $\ln(D(20,w))$ was plotted against $1/T$ an average activation energy of 3.8 ± 0.6 kJ mol^{-1} was obtained for aqueous solutions. This is less than was reported earlier[4] but still significantly greater than for thermal expansion of polystyrene (approximately 0.4 kJ mol^{-1}). It was also found that the angular dependence of $g^{(2)}(\tau)$ followed the expected linear relationship with $\sin^2(\theta)$ at all temperatures measured (extending up to 323K). It would be expected that if aggregation occurred at raised temperatures this would change the dependence from a linear one to a non-linear angular dependence. However, since we are measuring comparatively small changes in $D(20,w)$, this angular method is too insensitive to be helpful.

The decrease in $D(20,w)$ with rising temperature was observed in water, 0.1 M phosphate buffers at pH 7.2 and pH 8 and 0.1 M solutions of Na_2CO_3, Li_2CO_3, NaCl and LiCl (*Figure 1*). The average $D(20,w)$ from nine estimates made in these solutions was $(3.59 \pm 0.25) \times 10^{-12}$ m^2 s^{-1}, which corresponds to a solvated radius of 0.059 ± 0.004 μm (expected radius was 0.0545 μm). A true correspondence between our estimate and that given by the manufacturer of the polystyrene latex occurred at 288K. The addition of 0.06% (v/v) of Triton X-100 (a neutral detergent) considerably reduced the dependence (*Figure 1*) without significantly affecting the value at 293K (the absolute value was $(3.81 \pm 0.09) \times 10^{-12}$ m^2 s^{-1}). Similar reductions in the temperature dependence were observed when samples were prepared in phosphate buffer which had been stored at room temperature for several weeks but not if millimolar NaN_3 was present in the buffers. These observations indicate that small quantities of surface active agents can destroy the dependence, and the effects observed in stored phosphate must be caused by bacterial growth in the buffer. Loss of the dependence was also observed if the distilled water stood in a room where dimethyl ketone was used (*Figure 2*). It should be noted that even at low concentrations of ketone (0.01%) the slopes of $D(T)/D(20,w)$ against T were considerably reduced compared with water while at 0.1% the trend approximated to that expected for thermal expansion of the beads (*Figure 2*). The partition of dimethyl ketone between water and polystyrene strongly favours accumulation in the polystyrene, so although raising the tempera-
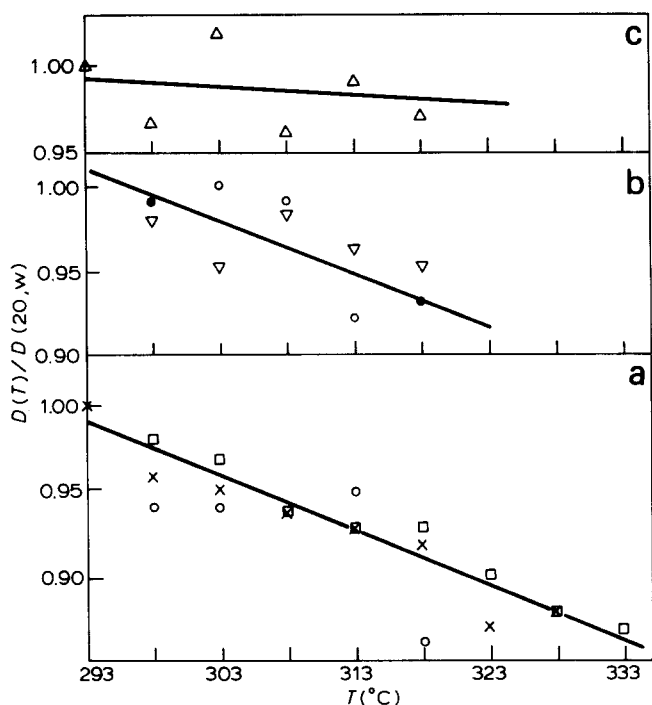
Figure 1 The dependence of $D(T)/D(20,\ w)$ on temperature (T) for a range of solvents $(D(T)$ is the diffusion coefficient normalized to 293 K for RT and viscosity of solvent): (a) X, H_2O; $\square$, 0.1 M phosphate buffer pH 7.2; O, buffer pH 8; (b) $\blacklozenge$, 0.1 M Na_2CO_3; $\bullet$, 0.05 M Na_2CO_3; (c) $\triangle$, 0.06% (v/v) Triton X-100. The average value for $D(20,\ w)$ measured at 293 K was $(3.59 \pm 0.25) \times 10^{-12}$ m^2 s^{-1}. Parameters from a linear regression were used to generate the lines associated with each set of data

ture reduces the concentration of ketone in water there will still remain a high concentration in the polystyrene even at relatively high temperatures. These results possibly point to the cause for the absence of this phenomenon reported by some workers[9] using distilled water, since distillation will steam distil neutral surface active agents and so concentrate the agent in distilled water having low conductivity.

In an attempt to clarify the solvent effects further the temperature dependence was measured for polystyrene in methanol and ethanol (*Figure 2*). There was a marked reduction in the dependence when measured in pure ethanol compared with water and the values of $D(20,\ w)$ correspond very closely with that expected for a sphere of radius 0.0545 nm: $D(20,\ w)$ for this sphere would be 3.88×10^{-12} m^2 s^{-1} and the experimental value is 3.83×10^{-12} m^2 s^{-1}. However, this effect was not found for solutions in pure methanol where the temperature dependence was greater than for water (activation energy in methanol was 6.4 kJ mol^{-1}). Furthermore in this solvent the absolute value of $D(20,w)$ at 293K was considerably less than for water when allowances were made for differences in viscosity $(D(20,w) = 1.71 \times 10^{-12}$ m^2 $s^{-1})$: this would correspond approximately to a stable 11-mer! It was found that the $D(20,w)$ of latex in solutions of 0.1 M LiCl showed little dependence on temperature and gave values for $D(20,w)$ at 293K similar to that found for water at this temperature.

The possibility of instrumental aberrations causing these results can be excluded since similar results were obtained using our equipment and the spectrometer at

Malvern Instruments Ltd (*Table 1*). The temperature dependence was retained for the two sets of data and the mean radius (five estimates) of the latex at 293K calculated from the Malvern data was 0.058 ± 0.002 μm, which corresponded very closely with the value obtained at Birmingham.

Oligomerization

A decrease in $D(20,w)$ with rising temperature could be caused by a small increase in the aggregation of the latex. It should be noted that the Malvern results were calculated using cumulants[8] and these ratios did not show any significant contribution from aggregates. Furthermore, this ratio did not change consistently or significantly with rising temperature (*Table 1*). Provencher's analytical procedure[6] provides an additional test for multicomponent relaxation curves as well as providing reliable estimates of the diffusion coefficient for the major component. In order qualitatively to assess the results from the many analyses made using DESCRETE, we calculated the ratio of the number of significant two-component systems detected by DESCRETE to the total number of accumulations analysed for each temperature. It should be mentioned that the two-component fits always produced values for the coefficients of the second component which had standard errors considerably lar-
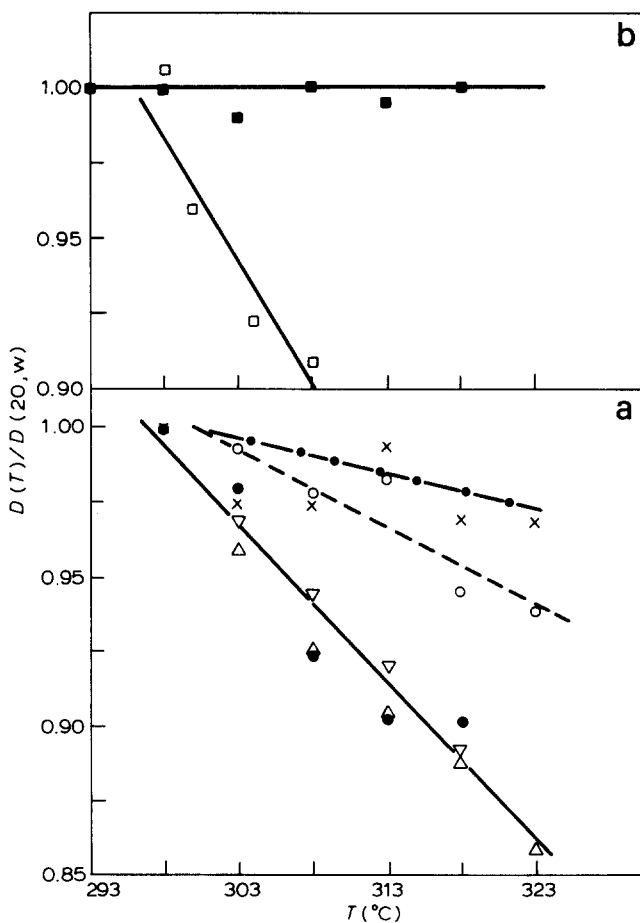

Figure 2 The dependence of $D(T)/D(20,\ w)$ (defined in *Figure 1*) on temperature for aqueous solutions of (a) dimethyl ketone and (b) alcohols. (a) The concentrations of dimethyl ketone (v/v) were: $\bullet$, $\triangledown$, 0; $\triangle$, 0.005%; O, 0.01%; X, 0.1% (b) Alcohols are: $\square$, MeOH; $\blacksquare$, EtOH. The parameters from a linear regression were used to generate the lines associated with each set of data

ger than the coefficient. Nevertheless the differences in total residuals between single- and double-exponential models were significant. The ratios given in *Table 2* show that single exponentials fitted data obtained in water, Triton X-100, 0.1 M Na$_2$CO$_3$, LiCl and 0.1 M K$_2$CO$_3$ while two-exponential models applied to 0.1 M KCl, NaCl and Li$_2$CO$_3$: there was never a need to expand beyond a two-exponential model. Often the proportion of significant two-exponential models increased at raised temperatures. The results for 0.1 M phosphate buffer pH 7.2 illustrates this effect since single exponentials were dominant below 313K but two exponentials became more significant at higher temperatures. It was also found that the temperature dependence for the latex in phosphate buffer was retained at temperatures where a two-component model was most significant. The test required using the monomeric $D(20,w)$ from the two-exponential model.

The data from methanol fitted a single exponential at all temperatures while those for ethanol fitted multi-exponential models at all temperatures.

A further method based on cumulant analyses[7,8] was employed to test whether polydispersity changed with temperature for the data collected at Malvern. The results given in *Table 1* for this analysis confirm that there was no detectable change in the estimated polydispersity with rising temperature for latex in water: similar conclusions were drawn for these data when analysed by DESCRETE and for other sets of data in water (*Table 2*). The polydispersity (P) (*Table 1*) calculated by cumulants is a measure of the width of the distribution, and arithmetical rounding errors that accumulate during the calculations limit the lower estimate for the second cumulant[7] to about

Table 3 Relative values of the diffusion coefficients $(D(20,w)(T)/D(20,w)(293))$ for polystyrene latex in 0.1 M NaCl at a range of temperatures (T). Analysis of the data using DESCRETE showed that a two-component model was the most significant (*Table 2*) so the diffusion coefficients for the latex were calculated from a single-component (A) and from the two-component (B) fit. The values of $D(20,w)$ for latex from a two-component fit were about 20% higher than for a single component but they carried standard errors of about 75% of the parameters

T (°C)	$D(20,w)(T)/D20,w)(293)$	
	(A)	(B)
293	1	1
298	0.91	0.95
303	0.89	0.91
308	0.88	0.90
313	0.86	0.83
318	0.84	0.88

0.01. Thus, the low values for P in *Table 1* indicate a very narrow distribution, which confirms the spread given in the supplier's specification of the latex (quoted value was ± 0.06 nm for a radius of 54.5 nm and this would correspond to a polydispersity of about 0.05).

The question remains as to whether the diffusion of latex particles as found from a significant two-component fit still showed a residual temperature dependence. This appeared to be the case although exact analyses were affected by the increased errors on the fitted coefficients in a two-component compared with a single-component fit. A typical example of the trends in the relative diffusion coefficients can be seen for a solution in 0.1 M NaCl (*Table 3*) where at all the temperatures a significant two-component fit was recorded. (*Table 2*). There was more variation between temperatures for the $D(20,w)$ taken from the two-component model (*Table 3*) but the trend of decreasing normalized diffusion coefficient with rising temperature remained. Considering the errors the ratios were satisfactorily similar for the two models.

It should be remembered that light scattering is relatively insensitive to polydispersity, but results from the two tests suggested that changing polydispersity could not account for the major part of the residual temperature dependence. It was necessary to set a limit on the sensitivity in our hands of the tests for polydispersity made by DESCRETE so simulated light scattering data were generated and analysed (*Table 4*). One set of tests was made on data which were accurate (within the limits of the rounding errors) and the other contained random errors carrying variances determined by a Poisson distribution similar to those generated by experimental procedures.

Table 1 A comparison between two independent estimates of $D(T)/D(25,w)$ [$D(T)$ being the diffusion coefficient normalized to 298°C but measured at T] for polystyrene latex in water. Polydispersity (P) was calculated by cumulants[7,8] for the Malvern data

T (°C)	$D(T)/D(25,w)$		P
	(A)	(B)	
298	1	1	0.051
303	0.99	0.98	0.061
308	0.98	0.96	0.057
313	0.97	0.95	0.034
318	0.96	0.94	0.040

(A) Collected in Birmingham (calculated radius at 293 K was 0.059 ± 0.004 μm)
(B) Collected at Malvern Instruments Ltd. (radius at 293 K was 0.058 ± 0.002 μm)

Table 2 The ratio of significant two-exponential models compared with the total number of accumulations for a set of temperatures. The salt solutions were all 0.1 M and the concentration of Triton X-100 was 0.06% (v/v)

T (K)	H$_2$O	Na$_2$CO$_3$	K$_2$CO$_3$	Triton	LiCl	HPO$_4^{2'}$	KCl	NaCl	Li$_2$CO$_3$
293	0	0	0	0	0	0	0	0.5	0.66
298	0	0	0	0	0	0	0.5	0.5	0.25
303	0	0	0	0	0	0	0.2	0.5	0.75
308	0	0	0	0	0	0	0.33	0.66	0.25
313	0	0	0	0	0	0.33	0.6	1.0	0
318	0	0	0	0	0	0.25	0.5	—	0.75
323	0	—	0	0	—	0.66	—	—	—
328	—	—	—	—	—	0.75	—	—	—
333	—	—	—	—	—	0.66	—	—	—

Table 4 Tests of sensitivity of DESCRETE for detecting dimerization using simulated data. The data were generated for a two-component system either without (A) or with (B) random errors. The errors were generated assuming a Poisson distribution for a total count of 10^6. This gives an average expected signal-to-noise ratio S/N of 10^2. The arguments for the two exponentials (i) used to calculate the data were 0.13 and 0.1, which would be equivalent to a sphere of radius 54 nm and its dimer. The amplitudes, which represent the relative proportions, were varied while keeping that of the monomer constant ($A(1) = 10^6$). A significant baseline (BL) was added in one case and is similar in magnitude to that found experimentally

Expected			Found							
BL	S/N	A_2	BL		S/N	λ_1	λ_2	A_1	A_2	No.
0	0	10^5	−0.33	± 0.31	5.94E4	0.1290 ± 0.0002	0.08997 ± 0.0037	1.051E6 ± 1.1E4	4.93E4 ± 1.10E4	2
0	0	10^4	−8.56	± 6.30	3.19E5	0.1298 ± 0.0003	0.0813 ± 0.0062	1.007E6 ± 8.9E2	3.081E3 ± 8.9E2	2
0	0	10^3	−1.202	± 1.10	—	0.1300 ± 3.0E − 6	0.0746 ± 0.0092	1.001E6 ± 8.5E1	2.236E2 ± 84	2
0	10^2	10^5	260.5	± 160	3.89E3	0.1253 ± 0.012	0.2015 ± 0.062	1.064E6 ± 4.4E4	3.656E4 ± 4.4E4	2
0	10^2	10^4	46.28	± 73.05	3.866E3	0.1296 ± 1.1E − 4	0.643 ± 0.480	1.009E6 ± 1.1E3	2.785E3 ± 9.6E2	2
0	10^2	10^3	−5.63	± 71.0	3.673E3	0.1299 ± 1.1E − 4	0.713 ± 0.65	1.00E6 ± 9.3E2	2.313E3 ± 1.0E3	2
10^5	10^2	10^5	1.00E5 ± 1.1E2		2.477E3	0.127 ± 7.6E − 5	—	1.098E6 ± 3.5E2	--	1

These tests showed that when the baseline was zero the tests always detected the two components and the values for both the amplitudes and the arguments of the one component were acceptable. This was not true, however, for the second component (the values for the coefficient and amplitudes were chosen to equate with a monomer–dimer system). If the decrease in $D(20,w)$ found experimentally was caused by increasd quantities of dimer then a 4% decrease in $D(20,w)$ would require an increase of about 10% dimer to the system (i.e. $A_2 = 10^5$, *Table 4*). Adding a significant baseline to the noisy data confused the tests and it seemed that a single-component model was significant although the parameters also calculated for a two-component model gave the expected parameters. Thus, it is possible that our inability to detect two components (see *Table 2*) was caused by high baselines in those samples. This argument can be countered by the fact that the number of counts collected was similar for all experiments and yet in some cases two-component models were the major result of the analyses (e.g. NaCl and Li_2CO_3, *Table 2*). It seems possible, therefore, that levels of oligomerization must have been greater in the two-component results than in those where a single model fitted. Furthermore, it seems that any insufficiencies in our analyses or treatment of solution which gave rise to a single model did not change with rising temperature and so could not account for the residual temperature dependence of $D(20,w)$.

DISCUSSION AND CONCLUSIONS

When the temperature of dilute solutions of polystyrene latex was increased there occurred a concomitant decrease in the normalized diffusion coefficient. This effect could be removed by adding a detergent (X-100) and dilute dimethyl ketone to the solutions but, in general, not by salts. The effect was enhanced when methanol but not when ethanol was used as the solvent. These observations qualitatively support earlier data[4] but showed that the level of the activation energy is probably smaller than originally calculated. The present value (3.8 kJ mol^{-1}) is probably more accurate since it is based on a more objective analysis of the experimental data. Use of the established procedures has shown that increased oligomerization at raised temperatures was not the major cause of the decreased diffusion. With large particles having small diffusion coefficients, like polystyrene latex, it is difficult to establish with certainty the degree of

heterogeneity in a solution. Other procedures such as centrifugation are not satisfactory experimental procedures. Thus, despite its relative insensitivity, quasielastic light scattering remains the best procedure especially when coupled to suitable fitting procedures. The present data showed that although in some solvents the oligomerization may increase with rising temperatures, it was not a common phenomenon and the decrease in the $D(20,w)$ occurred where no oligomerization could be detected. Furthermore, previous work[4] showed that there was no detectable hysteresis when the heated solutions were cooled back to the starting temperatures. This has been confirmed (but not reported here) and these results show that no irreversible interactions were occurring.

These factors make it increasingly likely that the decrease was caused by an increase in the solvated radius of the particle at increased temperatures. An increase of 10% in radius of a smooth sphere would mean that the average water-shell must increase by about eight layers of water at 320K compared with 290K and this seems excessive. However, the water will not be uniformly distributed but will be concentrated around the exposed charged groups embedded in the polystyrene. Since there are about 4000 charges per particle[10], this means that the sulphate groups occupy about 8% of the total surface area, the remaining area presumably being hydrophobic. Outgrowths of water layers from these centres would be in accord with potential energy calculations for hydrophobic amino acids[11] and the result would be a 'spiky' surface which would add considerably to the friction compared with a uniformly solvated sphere. Theoretical studies[12] show that the creation of a 'spiky' surface on a sphere considerably increases the translational drag but increases the average volume hardly at all. Thus, the number of extended solvation shells present at these areas would need to be considerably less than eight in order to reduce the diffusion coefficient to the extent measured here. If this is the explanation, then detergents and solvents soluble in polystyrene would fit between the charges and smooth the 'spiky' nature of the latex, so leading to a lowered frictional coefficient for the same number of water molecules adsorbed to the latex.

ACKNOWLEDGEMENTS

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