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ORIGINAL CONTRIBUTION

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Interparticle forces arising from an adsorbed strong polyelectrolyte in colloidal dispersions: charged patch attraction

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Abstract Adsorbed polystyrene sulphonate (PSS) shifts the pH of the zero zeta potential, $\mathrm{pH}_{\varsigma = 0}$, of ZrO_2 to a lower pH. The positive charge density of ZrO_2 at $\mathrm{pH} = \mathrm{pH}_{\varsigma=0}$ determined from the amount of PSS adsorbed was in excellent agreement with that obtained from charge titration. Polystyrene sulphonic acid shifts $\mathrm{pH}_{\varsigma=0}$ to a greater degree compared with polyacrylic acid because it is a much stronger acid. A patch is likely to just consist of one adsorbed molecule. The patch is negative when the charges of the molecule exceed the underlying positive surface charge. Attraction between the negative patch and the bare positive surface of a second particle is responsible for increasing the yield stress of concentrated ZrO_2 dispersions at $\mathrm{pH}_{\varsigma=0}$. Its magnitude is only of the order of the van der Waals attraction. Increasing ionic strength and patch misalignment diminish the attraction. The upper limit of the patch area was estimated from the radius of gyration of the molecule in solution. With a known patch area, the patch charged density can be calculated. With the selection of an appropriate patch area, the yield stress due to charged patch attraction increases linearly with the product of the negative and positive patch densities.

Key words Charged patch Interactions – Yield stress – Zeta potential – Dispersions – pH – Polysulphonic acid

Introduction

The importance of colloidal forces in the processing of dispersions is unquestionable. Forces in dispersions that have been reported are van der Waals [1, 2], electrostatic [1, 3], depletion [4, 5], steric [3, 6], bridging [7–12] and hydrophobic [13–16]. Steric, bridging and hydrophobic forces involve an adsorbed additive and the type of force is determined by the nature of the additives. Adsorbed small hydrophilic molecules such as citrate and phosphate form a hard wall steric layer which keeps the interacting particles further apart [3]. This results in a smaller yield stress at the pH of the zero zeta potential, $\mathrm{pH}_{\varsigma=0}$. Bolaform surfactants form highly directed bridging interactions which can cause up to a tenfold increase in the strength of the attraction [12]. A single head group surfactant gives rise to the strong "hydrophobic" force and a sixfold increase in attraction was recorded [15]. Here we present rheological results of yet another surface force, charged patch attraction, arising from an adsorbed strong polyelectrolyte. There are currently no experimental data for such interactions in dispersions.

A negatively charged patch is formed when the charge of the adsorbed anionic polyelectrolyte molecule exceeds the underlying positive surface charge in an area occupied by the molecule. Miklavic et al. [17] proposed a quantitative charged patch interaction model as a possible explanation for the relatively strong long-range hydrophobic force [18–22]. This model, however, fails to explain the insensitivity of the short-range component of the hydrophobic force to ionic strength [15, 22]. Moreover the predicted strength of the charged patch attraction is only of the same order of magnitude as the van der Waals attraction. A strong influence of ionic strength and patch properties such as potential, alignments, shape and sizes was also predicted.

Charged patch attraction was first proposed qualitatively by Gregory [23, 24] to explain the flocculation of his colloidal dispersions by a high-molecular-weight cationic polyelectrolyte. It is an attraction between a positive patch containing the adsorbed polyelectrolyte and a bare negative patch of a second particle. At rest the interacting particles must be at the state of minimum free energy or maximum attractive energy. This means that the negative and positive patches are in perfect alignment.

In this study the strong polyelectrolyte used was polystyrene sulphonate (PSS). Its acid form has a pK_a of 1.0 [25] or −1.34 according to Dinius and Chopin [26].

Materials and methods

The ZrO_2 powder had a BET surface area of 18.0 m^2/g. The particle size distribution measured with a coulter LS230 is characterized by a D_{90} of 0.53 μm, a D_{50} of 0.24 μm, and a D_{10} of 0.13 μm. Poly(4-styrene sulphonic acid) salt of sodium (PSS) was obtained from Aldrich as a 20 wt% solution. It has a molecular weight, M_w, of 110 000. M_w was calculated by comparing the viscosity with similar solutions for PSS of M_w 70 000 and 1 000 000 (also from Aldrich) and by assuming a power law relationship between viscosity and M_w.

In the preparation of a suspension, PSS was first dissolved in "Milli-Q" water containing one or two drops of 8 M NaOH solution before the addition of ZrO_2 powder. The mixture was sonicated for a period of 1 min with the probe of a Branson sonifier. The resultant suspension was generally dispersed and homogeneous.

Concentrated nitric acid (1–15.8 M) was used to change the dispersion pH so as to minimize dilution. Localised flocculation was observed in the vicinity of the acid droplets and was redispersed by sonication. After each pH change the dispersion was rested for 2 h and then stirred vigorously with a spatula before the yield stress measurement.

Results and discussion

Surface properties

The effect of the polystyrene sulphonate salt of sodium (PSS) concentration on the zeta potential-pH behaviour of ZrO_2 is shown in Fig. 1. An isoelectric point (IEP) was observed at pH 7.8 ± 0.3 for ZrO_2. Adsorbed PSS shifts the pH of the zero zeta potential, $\mathrm{pH}_{\varsigma=0}$, to a lower pH. $\mathrm{pH}_{\varsigma=0}$ is 6.0, 4.4 and 2.9 for 0.11, 0.2 and 0.34 dwb% (g/100g ZrO_2) PSS respectively. No $\mathrm{pH}_{\varsigma=0}$ was observed for 0.5 and 1.0 dwb% PSS despite going as low as pH 1.5. The zeta potential remains negative even at this pH. However, both 0.5 and 1.0 dwb% PSS exhibited a minimum (magnitude wise) negative potential, both occurring at the same pH of 2.0. The minimum negative potential is very low for the 0.5 dwb% PSS: it is only −5 mV, whereas for the 1.0 dwb% additive it is −35 mV.

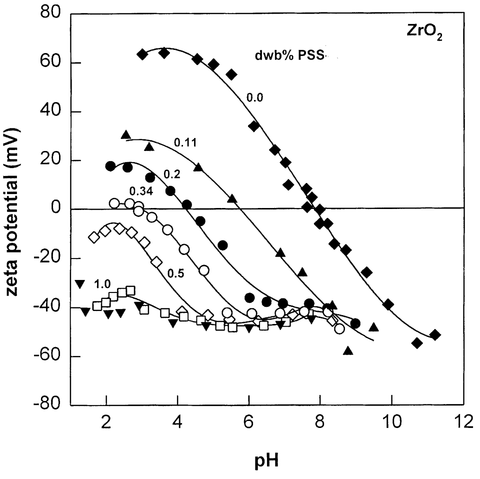


Fig. 1 The effect poly[sodium 4-styrene sulphonate] or polystyrene sulphonate (*PSS*) concentration on the zeta potential-pH behaviour of a ZrO_2 dispersion

At pH = $\mathrm{pH}_{\varsigma=0}$ the negative charge from the adsorbed PSS must equal that of the positive surface charge. Thus, by knowing the amount of PSS adsorbed the positive surface charge density of ZrO_2, σ_o, at pH = $\mathrm{pH}_{\varsigma=0}$, can be calculated. The task of determining σ_o is made even easier by two factors; firstly adsorption like for polyacrylic acid (PAA) [11] is almost 100% at pH = $\mathrm{pH}_{\varsigma=0}$ and secondly PSS is completely dissociated or fully charged at a pH greater than 2.0.

Hence the equation for calculating σ_o at pH = $\mathrm{pH}_{\varsigma=0}$ is

$$\sigma_o = -\sigma_{PSS} = -\frac{mN_Ae}{A_S} ,$$

where σ_{PSS} is the charge density due to adsorbed PSS, m is the total moles of the repeating unit of PSS, N_A is Avogadro's number, e is the electronic charge and A_S is the total surface area of ZrO_2. Only three σ_o data were obtained as only 0.11, 0.2 and 0.34 dwb% PSS exhibited a $\mathrm{pH}_{\varsigma=0}$.

These σ_o data, plotted in Fig. 2, compared well with those obtained from charge titration with a standard KOH solution. The charge titration data were obtained at 10^{-3} M KNO_3. After titration the ionic strength would be of the order of 0.01 M. Note that this polyelectrolyte adsorption and $\mathrm{pH}_{\varsigma=0}$ method for determining σ_o does not work for the relatively week polyacrylic acid [11].

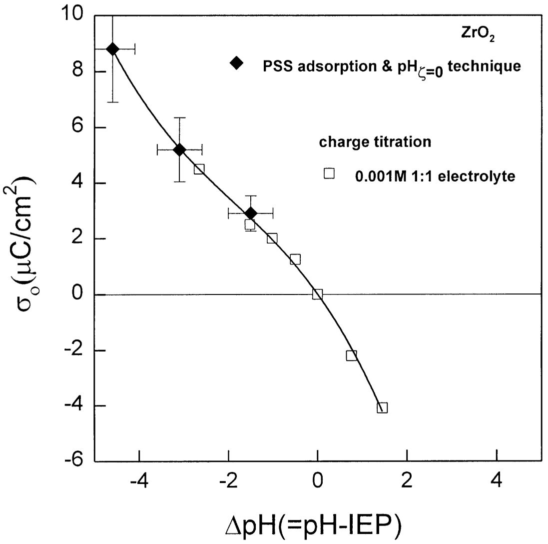


Fig. 2 Plot of surface charge density versus $\Delta pH(=pH-IEP)$ for ZrO_2 obtained by charge titration and a combination of PSS adsorption and $pH_{\varsigma=0}$ technique

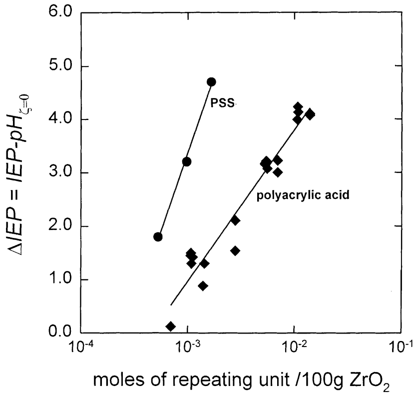


Fig. 3 Plot of ΔIEP versus log of repeating unit concentration for PSS and polyacrylic acid showing a linear relationship for both polyelectrolytes

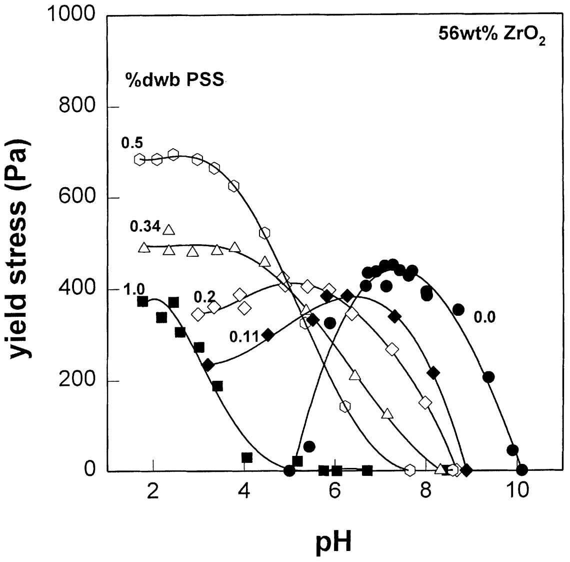


Fig. 4 The effect of poly[sodium 4-styrene sulphonate] or PSS concentration on the yield stress-pH behaviour of a 56 wt% ZrO_2 suspension

A plot of $\Delta IEP(=IEP - pH_{\varsigma=0})$ versus $\log c_{rpt}$ for both PSS and PAA [11] is shown in Fig. 3. c_{rpt} is the repeating unit concentration in mole/100 g ZrO_2. A linear relationship is obtained for both polyelectrolytes but the gradient is much steeper for PSS. Using a linear regression technique, the relationship between ΔIEP and c_{rpt} obtained for PSS is:

$$\Delta IEP = 5.83 \log c_{rpt} + 20.86$$

for c_{rpt} ranging from 5.24×10^{-4} to 1.65×10^{-3} mol/100g ZrO_2. In comparison, the relationship for PAA is

$$\Delta IEP = 2.83 \log c_{rpt} + 9.47 \ .$$

The steeper slope for PSS means that for a given repeating unit concentration, PSS shifts $pH_{\varsigma=0}$ to a greater degree. This is because polystyrene sulphonic acid is a much stronger acid. It has a pK_a of less than 1.0 [25]. In comparison the pK_a for PAA is 5.0 [27]. Thus at pH 2.0 the PSS molecule is fully charged whereas the PAA molecule is virtually neutral. Note that the PAA molecular weight was found to have no effect on the value of $pH_{\varsigma=0}$ [11].

Yield stress

The effects of PSS concentration on the yield stress-pH behaviour of a 56 wt% ZrO_2 suspension are shown in Fig. 4. PSS shifts the yield stress curve to a lower pH. In the absence of PSS a typically parabolic shaped curve is obtained with a maximum yield value of 450 Pa. PSS, however, caused the curve to become relatively flat at the maximum yield value. A similar feature was observed for fatty acid additives [15].

Initially the maximum yield stress shows a small decrease at a low concentration of 0.11 dwb% PSS. It begins to increase upon increasing the PSS concentration. The largest maximum yield of 700 Pa was recorded for 0.5 dwb%. Then it decreases again to 380 Pa at 1.0 dwb%. The ionic strength, calculated based on the amount of nitric acid added to get to the maximum yield was of the order of 0.01 M (1:1 electrolyte) for all suspensions.

The maximum yield stress for 0.11, 0.2 and 0.34 dwb% PSS occurred in the pH region where $pH_{\varsigma=0}$ is located. For 0.5 and 1.0 dwb% PSS the maximum yield was found to correspond to the minimum (negative) potential state, i.e. −5 mV for

0.5 dwb% PSS and −35 mV for 1.0 dwb%. The smaller maximum for the 1.0 dwb% PSS is entirely consistent with the much larger minimum (negative) potential observed.

An additional attractive force must be present to account for the much larger maximum yield stress arising from adsorbed PSS. This is attributed to charged patch attraction. The negatively charged patches formed by adsorbed PSS are attracted to the positive ZrO_2 surface of a second particle. At $pH_{\zeta=0}$ there are three forces of interaction which contribute to the maximum yield stress: van der Waals, steric and charged patch attraction. The steric component is always present because of the physical layer formed by the adsorbed PSS. The steric and van der Waals contributions were assumed to be equal to the maximum yield stress [11] for adsorbed PAA at the same surface coverage. Thus, the charged patch attraction contribution to the maximum yield stress, $\tau_{y_{cp}}$, can be determined. $\tau_{y_{cp}}$ versus PSS concentration, c in g/100 g ZrO_2, is plotted in Fig. 5. It shows that $\tau_{y_{cp}}$ increases linearly with PSS concentration. Using a linear regression technique one obtains

$$\tau_{y_{cp}} = 905c$$

for c ranging from 0 to 0.5 g/100 g ZrO_2. Data for 0.5 dwb% PSS were also included in the plot because of the near zero zeta potential condition at the maximum yield stress.

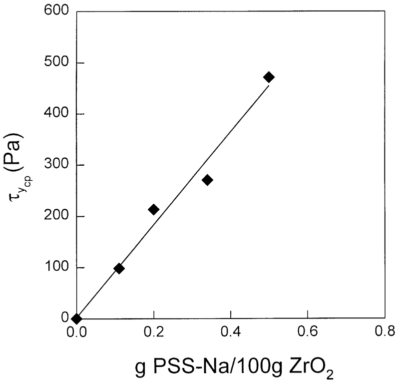


Fig. 5 Plot of charged patch attraction contribution to the maximum yield stress versus PSS concentration for ZrO_2 dispersions showing a linear relationship. PSS-Na in the plot is equivalent to PSS

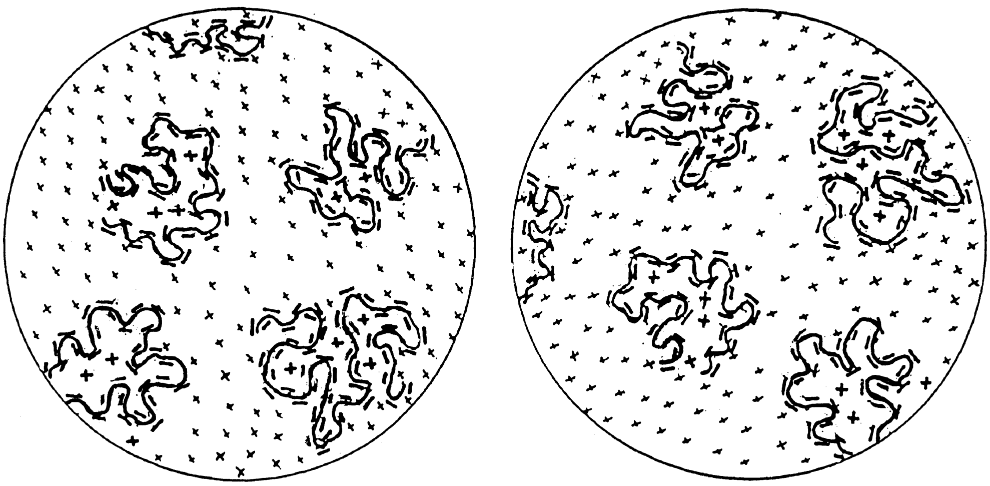
A representation of charged patch interaction between two particles is shown in Fig. 6. The particles are shown to contain patches formed by adsorbed PSS molecules. At the closest point of interaction it can be seen that an adsorbed (negative) patch directly faces a bare (positive) patch.

The degree of surface coverage and ionic strength are expected to have a significant effect on charged patch attraction. At high surface coverage, the fraction of bare positive patches will be greatly diminished. At monolayer coverage, charged patch interaction is essentially nonexistent. High ionic strengths shield the charges on the patch thereby diminishing the attraction. Other factors that affect this attraction are the size and shape, the potential and the alignment of the patches [17]. These parameters are generally very difficult to characterize experimentally.

Assuming 100% adsorption the surface coverage for 0.11, 0.2, 0.34, 0.5 and 1.0 dwb% PSS is 475, 257, 151, 103 and 51 Å^2 per repeating unit, respectively. Based on a monolayer coverage for sodium dodecyl sulphonate of 30 Å^2 per molecule [28], the surface coverage is 6.3, 12, 20, 29 and 59%, respectively. The actual surface coverage is certainly larger as the area occupied by a repeating unit is larger than the sulphonate head group area.

The effect of ionic strength on the yield stress-pH behaviour for the ZrO_2 suspension containing 0.34 dwb% PSS is shown in Fig. 7. Two ionic strengths,

Fig. 6 An illustration of charged patch interaction between two particles. It can be seen that a polyelectrolyte (negative) patch faces a bare (positive) patch at the closest distance of interaction



0.05 and 0.5 M KNO_3, were evaluated. The effect is quite pronounced as indicated by the large decrease in the maximum yield stress from 500 to 270 Pa as the ionic strength increases from 0.05 to 0.5 M. The theory of polyelectrolyte adsorption on an oppositely charged surface predicts that the adsorbed PSS will adopt a flat configuration at low to moderate ionic strength [29]. However, at high ionic strength the polymer will adopt an extended configuration which favours conventional bridging. The lower maximum yield stress at high ionic strength suggests that bridging forces are not important.

The misalignment between the positive and negative patches will reduce the attraction [17]. Figure 8 shows the effect of vane rotational speed on the maximum yield stress. The faster the rotation the greater the degree of misalignment. The results show the yield stress decreases with increasing speed of rotation which is entirely consistent with the misalignment effect.

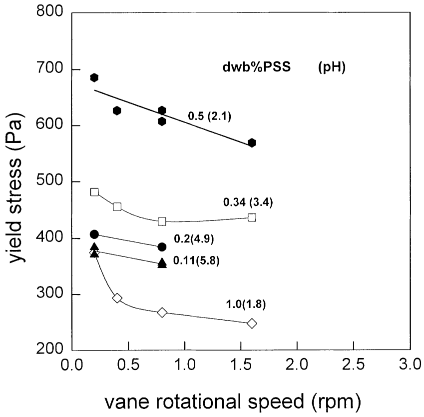


Fig. 8 The effect of vane rotational speed on the yield stress of a ZrO_2 dispersion

Charged patch interactions

The size or conformation of the PSS molecule in solution can give an indication of the patch size formed when it is adsorbed on the particle surface. The unperturbed root mean square end-to-end distance, r_o, of a linear poly(styrene-*p*-sulfonic acid) molecule (sodium salt) in aqueous 4.17 M NaCl solution is [30]

$$\left(\frac{r_o}{M_w^{1/2}}\right) \times 10^4 = 425 \text{ nm} .$$

The unperturbed radius of gyration is

$$R_g^\theta = \left(\frac{r_o^2}{6}\right)^{1/2} .$$

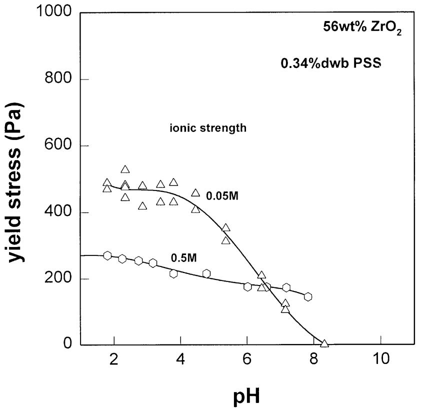


Fig. 7 The effect of ionic strength on the yield stress-pH behaviour of a 56 wt% ZrO_2 dispersion containing 0.34 dwb% PSS

For a PSS of $M_w = 110\,000$, r_o and R_g^θ are 14.1 and 5.8 nm. As the PSS is in a dilute salt solution, the molecule will be in an expanded configuration and the radius of gyration is related to the unperturbed dimension by

$$R_g = \alpha R_g^\theta ,$$

where α is the Flory or linear expansion factor. To obtain α the viscosity-based expansion factor, α_v, was first determined using the following equation [31]:

$$\alpha_v^3 = \frac{[\eta]}{[\eta]_\theta} = \frac{K M_w^a}{K_\theta M_w^{1/2}} .$$

Data for K and a at various ionic strengths are given in Kurata et al. [30]. α_v is related to α by [31]

$$\alpha_v^3 = \alpha^{2.43} .$$

Hence the R_g for *a* PSS molecule with $M_w = 110\,000$ is 16.4 nm in 0.01 M NaCl solution and 14.1 nm in 0.05 M solution.

For the calculation of charged patch density it is necessary to know the area of an average patch. As yet there is no established relationship between radius of gyration and patch area. Assuming that the patch consists of only one absorbed PSS molecule, the patch area, A_p, would be of the order of R_g^2. If the patch is circular with a radius $R_g(=16.4\,\text{nm})$ then A_p is 844 nm^2 or if it is a square with length R_g then A_p is 269 nm^2. The lower limit for A_p is 160 nm^2 calculated based on monolayer packing of the sulphonate group assuming an area of 30 Å^2 per head group [28].

Each patch contains 534 repeating units and each repeating unit contributes an electronic charge. Thus the smaller the patch area the higher the negative charged patch density, σ_{PSS} $(=534e/A_p)$. For A_p of 314 nm^2, σ_{PSS} is -27.2 $\mu C/cm^2$. The net charged patch density, σ_{cp}, is

$$|\sigma_{\mathrm{cp}}| = |\sigma_{\mathrm{PSS}}| - |\sigma_{\mathrm{o}}| \ .$$

$|\sigma_o|$ is known at $\mathrm{pH}_{\varsigma=0}$ for 0.11, 0.2 and 0.34 dwb% PSS and is 2.9, 5.2 and 8.8 μC/cm^2, respectively. Thus σ_{cp} at $\mathrm{pH}_{\varsigma=0}$ is −24.3, −22.0 and −18.4 μC/cm^2 (Table 1).

At rest, the interacting particles are at the state of maximum attractive energy. The negative patch is in perfect alignment with the positive (patch) bare surface of a second particle. The magnitude of the maximum attractive energy V_{cp} should therefore be proportional to the product of the charge density of the patches, i.e.

$$V_{\mathrm{cp}} \propto \tau_{\mathrm{y_{cp}}} \propto \sigma_{\mathrm{o}}\,\sigma_{\mathrm{cp}} \ .$$

The yield stress due to charged patch attraction (at $\mathrm{pH}_{\varsigma=0}$) must also be proportional to this product. The surface separation, the ionic strength, the patch alignment, etc., are assumed to be the same for all three PSS concentrations. Figure 9 shows the relationship between the yield stress due to charge patch attraction and the product of the charged density. A good linear relationship is clearly obtained for A_{p} of 314 and 201 nm^2 except for the last datum which is not at the zero zeta potential condition.

For optimum charged patch attraction there must be sufficient patches and bare surfaces for interactions. The results in Fig. 9 suggest that A_{p} of 625 nm^2 is probably an overestimate of the actual area. At 0.34 dwb% PSS the yield stress is still increasing and yet the product of the patch charge densities is smaller. Moreover, the total PSS patch area is rather high, 64.2% of the total surface area. This should also lead to a smaller yield stress as the area available for patch interactions is diminished.

For A_{p} of 314 nm^2 the linear relationship between the yield stress and the patch charge densities' product extends up to 0.34 dwb% PSS only. At this concentration the PSS patches occupied only 32.2% of the total surface area. There are therefore sufficient bare surfaces for patch interactions. At 0.5 dwb% PSS the increase in the yield stress with the charge density product is much larger. Here a rather high 50% of the total area is occupied by the PSS patches. It is possible that at high polymer concentrations A_{p} may be smaller than 314 nm^2 as the repulsion between PSS molecules tends to keep the patches far apart and this can only happen if the patch becomes smaller. If A_{p} decreases to 201 nm^2 then the linear relationship for A_{p} of 314 nm^2 will extend up to 0.5 dwb% PSS.

Table 1 Underlying surface and charged patch density (A_{p} = 314 nm^2) as a function of pH

dwb% PSS	$\mathrm{pH}_{\varsigma=0}$	σ_{o} (μC/cm^2)	σ_{PSS} (μC/cm^2)	σ_{cp} (μC/cm^2)
0.11	6.0	2.9	−27.2	−24.3
0.2	4.4	5.2	−27.2	−22.0
0.34	2.9	8.8	−27.2	−18.4

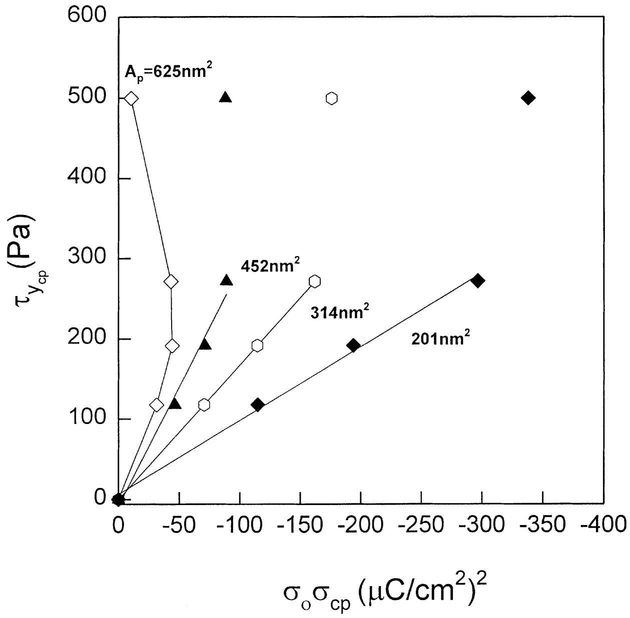


Fig. 9 The relationship between the charged patch attraction contribution to the maximum yield stress and the product of patch charge densities

Conclusion

1. A technique based on PSS adsorption and the pH of the zero zeta potential measurement can be used to determine the positive surface charge density of ZrO_2 as a function of pH.
2. PSS shifts the pH of the zero zeta potential to a greater degree compared with PAA because it is a much stronger acid.
3. Charged patch attraction clearly explains the larger maximum yield stress of ZrO_2 dispersions arising from adsorbed PSS. The charged patch contribution to the maximum yield stress increases linearly with PSS concentration in the range 0.0–0.5 g/100 g ZrO_2 and also with the product of the patch charge densities.

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