

# Ch 13

## Rheology of particulate gels

# Rheological measurements

On concentrated, strongly flocculated gels are hampered by the following difficulties

1. Poor reproducibility
2. Sensitivity to gel preparation
3. Sensitivity to shear history
4. Extermely limited range of linear viscoelastic response
5. Slip

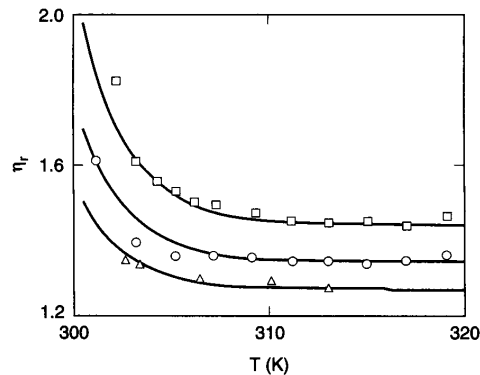
<- Particles bound strongly together in their primary van der Waals potential minima are unable to rearrange within lab time scales; hence the structures cannot relax to achieve thermodynamic equilibrium

-> gel structure depends on preparation histroy, including any deformation experienced by the gel prior to the rheological measurement

# Weakly flocculated gels

## Viscosity of thermoreversible gels

### at low concentration

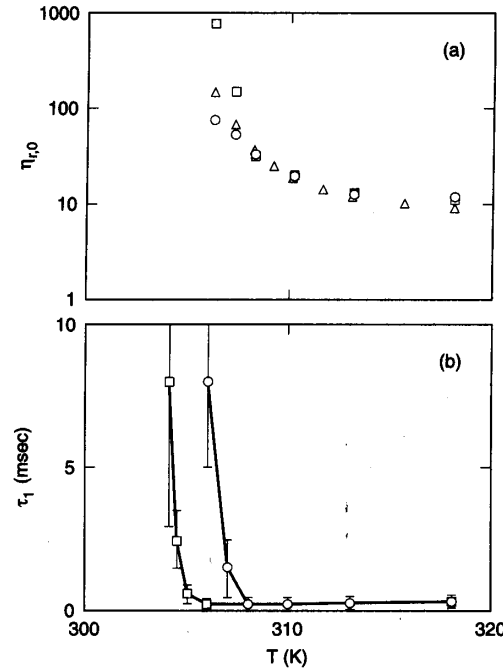


**Figure 7.6** Relative viscosity as a function of temperature  $T$  for dispersions in benzene of octadecyl-grafted silica spheres with radii  $a = 47$  nm at volume fractions  $\phi$  of 0.133 ( $\square$ ), 0.106 ( $\circ$ ), and 0.088 ( $\triangle$ ). The lines are the predictions of Eq. (7-21), with square well parameters of  $\Delta = 0.3$  nm,  $\alpha = 117$  and  $\theta = 316$  K. (From Woutersen and de Kruif, reprinted with permission from J. Chem. Phys. 94:5739, Copyright © 1991, American Institute of Physics.)

$$\eta_{r,0} = 1 + 2.5\phi + \left(6.2 + \frac{2.1}{\tau_B}\right)\phi^2$$

the viscosity increases exponentially with the depth of the potential well

### at high concentration



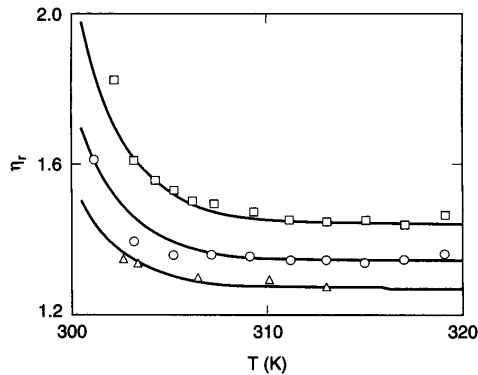
**Figure 7.7** (a) Relative viscosity as a function of temperature  $T$  for a dispersion described in Fig. 7-6 at a volume fraction  $\phi$  of 0.47, extrapolated to low shear rates ( $\circ$ ,  $\triangle$ ), and at low shear frequencies ( $\square$ ), from steady shearing and oscillatory shearing, respectively. (b) Longest relaxation time  $\tau_1$  as a function of temperature for  $\phi = 0.40$  ( $\square$ ) and 0.47 ( $\circ$ ). (From Woutersen et al., reprinted with permission from J. Chem. Phys. 101:542, Copyright © 1994, American Institute of Physics.)

$$\tau \approx \frac{a^2}{D_0} \exp\left(\frac{-\alpha W_{\min}}{k_B T}\right) = \frac{6\pi\eta_s a^3}{k_B T} \exp\left(\frac{-\alpha W_{\min}}{k_B T}\right)$$

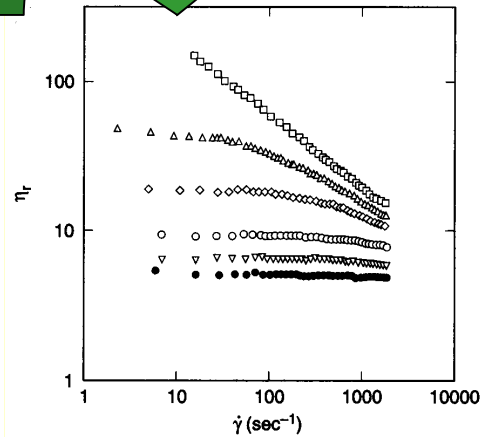
the more strongly a gel is flocculated, the longer it takes to reach thermodynamic equilibrium

# Weakly flocculated gels

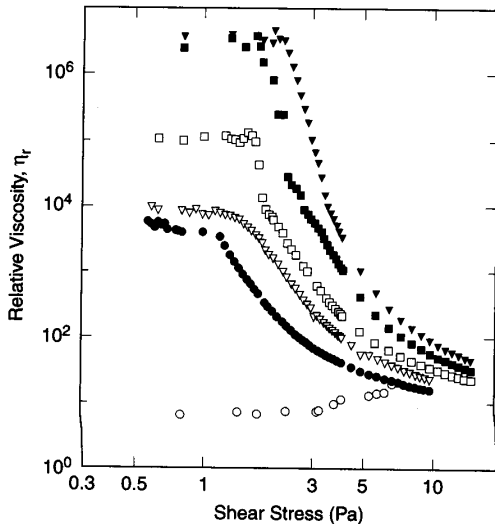
## Viscosity of thermoreversible gels



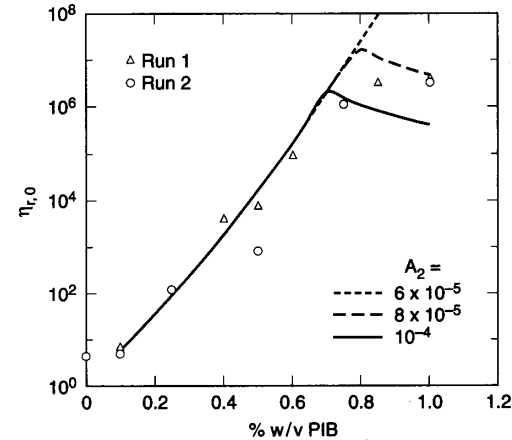
**Figure 7.6** Relative viscosity as a function of temperature  $T$  for dispersions in benzene of octadecyl-grafted silica spheres with radii  $a = 47$  nm at volume fractions  $\phi$  of 0.133 ( $\square$ ), 0.106 ( $\circ$ ), and 0.088 ( $\triangle$ ). The lines are the predictions of Eq. (7-21), with square well parameters of  $\Delta = 0.3$  nm,  $\alpha = 117$  and  $\theta = 316$  K. (From Woutersen and de Kruif, reprinted with permission from J. Chem. Phys. 94:5739, Copyright © 1991, American Institute of Physics.)



**Figure 7.8** Shear-rate dependence of the relative viscosity for a dispersion similar to that described in Fig. 7-6 at a volume fraction  $\phi$  of 0.367 and at temperatures (from bottom to top) of 317.28 K, 308.13 K, 306.20 K, 304.17 K, 303.16 K, and 302.16 K. (From Woutersen and de Kruif, reprinted with permission from J. Chem. Phys. 94:5739, Copyright © 1991, American Institute of Physics.)



**Figure 7.9** Shear-stress dependence of the relative viscosity for dispersions in "white spirit" of acrylic copolymer particles of radius  $a = 157$  nm at a volume fraction of  $\phi = 0.40$  for differing concentrations of non-adsorbing polyisobutylene polymer of molecular weight 411,000. The particles had been stabilized by addition of a comb-graft copolymer of PMMA backbone (which adsorbed to the particles) with non-adsorbing poly(12-hydroxystearic acid) teeth. The concentrations (in weight per unit volume) of polyisobutylene are 1.0% ( $\blacktriangledown$ ), 0.85% ( $\blacksquare$ ), 0.6% ( $\square$ ), 0.5% ( $\nabla$ ), 0.4% ( $\bullet$ ), and 0.1% ( $\circ$ ). (From Buscall et al. 1993, with permission from the Journal of Rheology.)

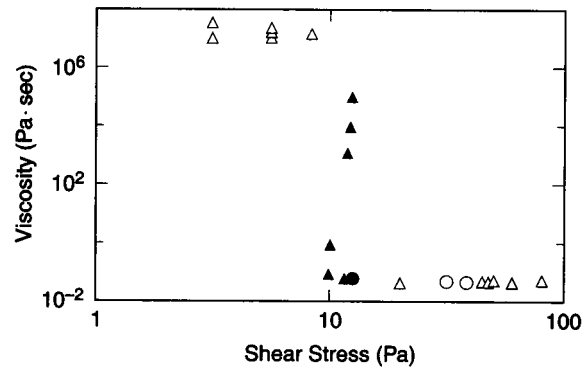


**Figure 7.10** The effect of polyisobutylene (PIB) concentration on the zero-shear viscosity of the suspensions described in Fig. 7-9. The lines were calculated assuming  $\eta_{r,0}(0) = K \exp(-\alpha W_{\min}/k_B T)$ , with values of the second virial coefficient  $A_2$  of  $6 \times 10^{-5}$ ,  $8 \times 10^{-5}$ , and  $10^{-4}$ . (From Buscall et al. 1993, with permission from the Journal of Rheology.)

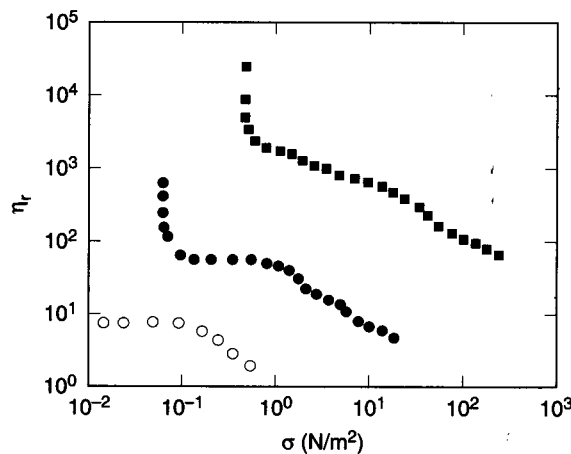
# Weakly flocculated gels

Yield stress;

as the gel becomes more flocculated, not only does the low shear rate plateau viscosity become larger, but the viscosity drop becomes steeper



**Figure 7.11** Viscosity versus shear stress for flocculated 2.5% silica particles in methyl laurate. The open triangles are from a stress-controlled instrument, while the other symbols are from a shear-rate-controlled one. (Reprinted from *Coll. Surf.*, 69:15, Van der Aerschot and Mewis (1992), with kind permission from Elsevier Science - NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands.)



**Figure 7.12** Shear-stress dependence of the relative viscosity for dispersions in water of charged polystyrene particles of radius  $a = 115$  nm with nonadsorbing Dextran T-500 polymer (synthesized from glucose) added as a depletion flocculant. The polymer molecular weight is 298,000, and its radius of gyration  $R_g$  is 15.8 nm. Volume fractions and polymer concentrations are:  $\phi = 0.3, C_p = 2.5$  wt% (■),  $\phi = 0.2, C_p = 2.5$  wt% (●), and  $\phi = 0.2, C_p = 0.5$  wt% (○). (From Patel and Russel 1987, with permission from the *Journal of Rheology*.)

# Strongly flocculated gels

Gels in which the attractive potential minimum is large  $-U_{\min} / k_B T \geq 20$

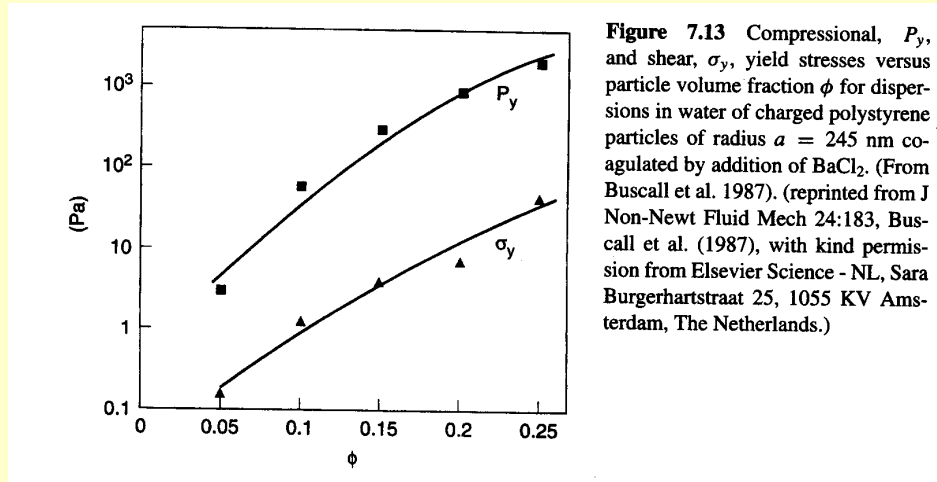
- > particle rearrangement are strongly suppressed
- > the time for equilibration of the structure is too long to occur within the experimental time frame

Rheological measurements are difficult

- > strongly flocculated suspensions are by definition **not at equilibrium**
- > properties are sensitive to preparation method and deformation history
- > multiple runs must be averaged
- > in large deformation or continuous shearing, slip is always a danger

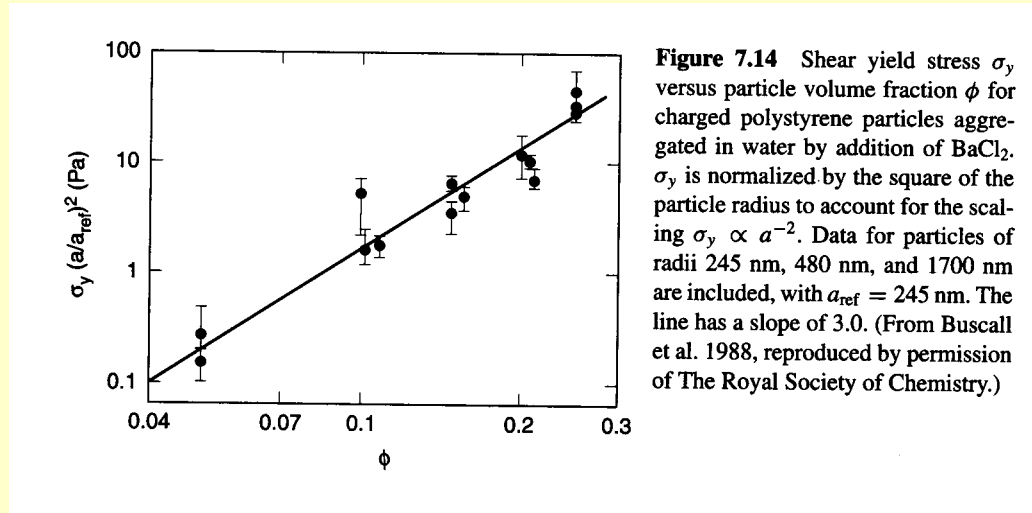
# Strongly flocculated gels

## Compressive and shear yield stresses



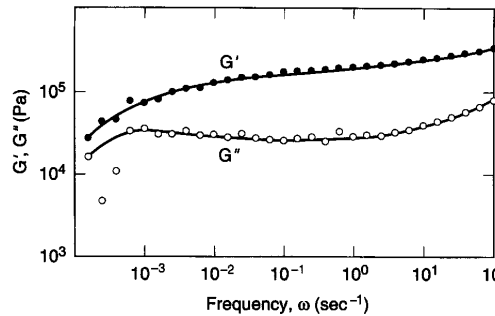
$$P_y \propto G_\infty \propto \phi^\mu$$

$$P_y \sim a^{-2.3}, \quad \sigma_y \sim a^{-2}$$

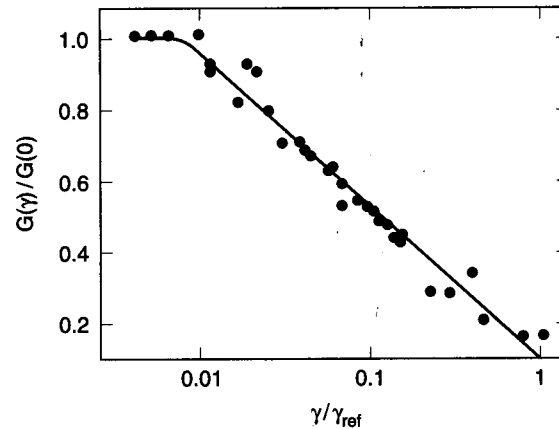


# Strongly flocculated gels

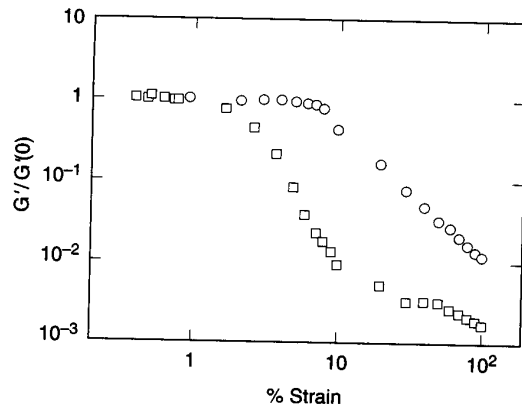
## Modulus



**Figure 7.15** Storage and loss moduli  $G'$  and  $G''$  as functions of frequency oscillatory straining at a strain amplitude of 0.5% for a silica particulate disp.  $a \approx 25$  nm) gelled by reduction of pH.



**Figure 7.16** Low-frequency shear modulus  $G(\gamma)$  divided by the small-amplitude modulus  $G(0)$ , versus normalized strain  $\gamma/\gamma_{ref}$  for charged polystyrene particles of radii  $a = 245$  nm and 1300 nm and volume fractions between 0.1 and 0.25 aggregated in water by addition of  $BaCl_2$ .  $\gamma_{ref}$  ranges from 0.015 to 0.073. (From Buscall et al. 1988, reproduced by permission of The Royal Society of Chemistry.)



**Figure 7.17** Shear elastic modulus  $G'(\gamma)$  divided by the small-strain modulus  $G'(0)$  versus strain  $\gamma$  for dispersions in hexadecane of octadecyl-grafted silica spheres with radius  $a = 56$  nm and concentration  $\phi = 0.182$ . The temperatures are 29°C (○), and 20°C (□). (From Chen and Russel 1991, reprinted with permission from Academic Press.)

at 29C, weakly flocculating

at 20C, strongly flocculating

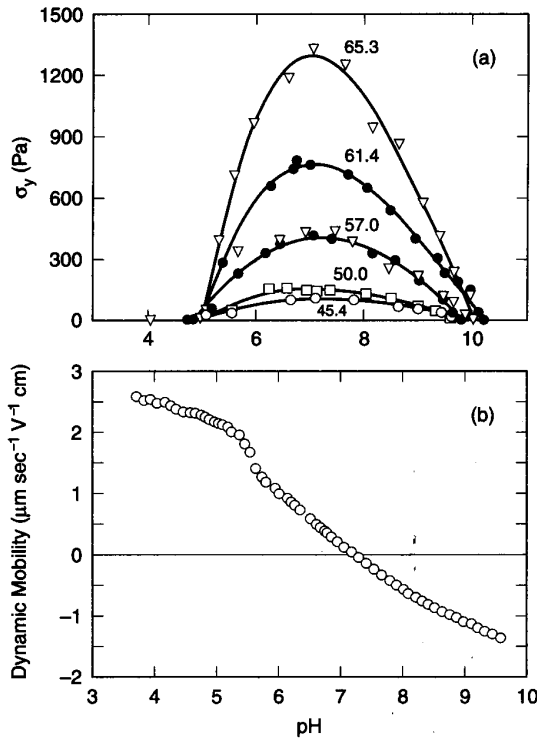
Strongly flocculating gels are more brittle



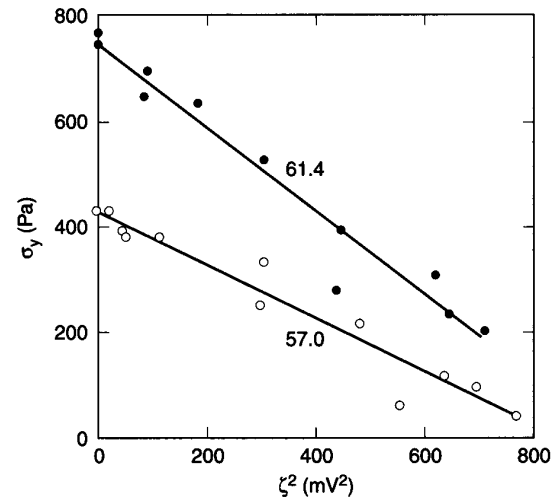
# Strongly flocculated gels

The mechanical properties of a gel depend not only on particle radius, concentration, but also on the flocculation strength

For gels in aqueous media, the properties depend on the charge on the particle surfaces as well as on the type of ions that might be bound to them

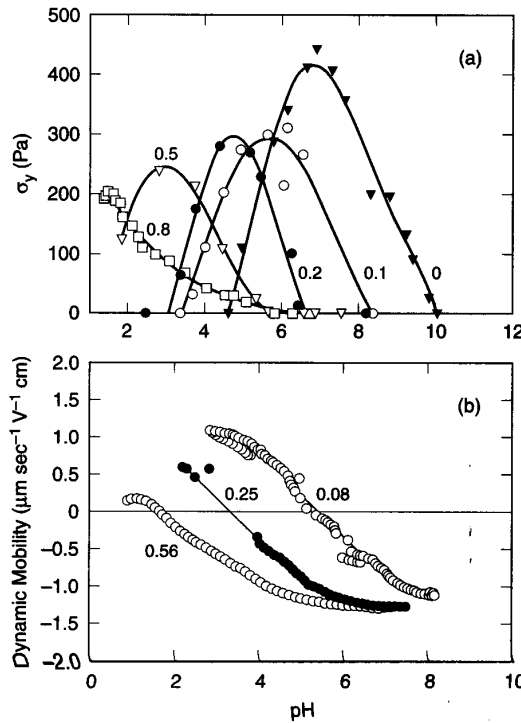


**Figure 7.18** (a) Shear yield stress  $\sigma_y$  versus pH for dispersions in water of “blocky”-shaped  $\text{ZrO}_2$  particles with radius  $a = 150$  nm and volume fractions  $\phi = 0.124, 0.145, 0.184, 0.213,$  and  $0.242$ . These correspond to the mass percentages 45.4%, 50.0%, 57.0%, 61.4%, and 65.3%. The pH was adjusted using  $\text{HNO}_3$  and  $\text{KOH}$ . (b) The dynamic mobility of particles in diluted suspensions as a function of pH. (From Leong et al. 1993, reproduced by permission of The Royal Society of Chemistry.)

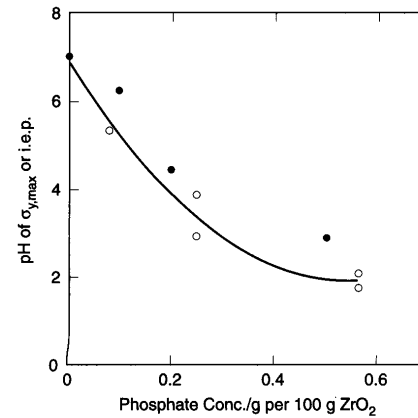


**Figure 7.19** Shear yield stress versus square of the zeta potential  $\zeta^2$  for the dispersions described in Fig. 7-18 at particle volume fractions  $\phi = 0.184$  and  $0.213$ , or mass percentages of 57.0% and 61.4%. The zeta potential was obtained at low  $\phi$  from the dynamic mobility. (From Leong et al. 1993, reproduced by permission of The Royal Society of Chemistry.)

# Strongly flocculated gels



**Figure 7.20** (a) Shear yield stress  $\sigma_y$  versus pH for dispersions described in Fig. 7-18 at a volume fraction  $\phi = 0.184$ , with varying amounts of added phosphate shown as a percentage on a dry weight basis. (b) The dynamic mobility of diluted ( $\phi = 0.025$ ) suspensions as a function of pH with varying amounts of added phosphate. (From Leong et al. 1993, reproduced by permission of The Royal Society of Chemistry.)



**Figure 7.21** pH at which the yield stress  $\sigma_y$  is maximum ( $\bullet$ ) and pH at the isoelectric point ( $\circ$ ) measured electroacoustically, versus concentration of phosphate, for suspensions described in Fig. 7-20. (From Leong et al. 1993, reproduced by permission of The Royal Society of Chemistry.)

Isoelectric point; pH at which zeta potential is zero

- The pH at which zeta potential can be adjusted by adding surface-binding anions
- As they are added, anions bind to the particle surface, rendering it more negatively charged; to neutralize this charge, pH should be lowered to supply  $\text{H}^+$  ions; thus the pH at isoelectric point is less when anions are present
  - > the pH at which yield stress is maximized is correspondingly reduced.
- The binding of ions increases the thickness of the hydration layers
  - > reduces the yield stress