

Colloidal Refractometry for Characterisation of Dispersions



Colloidal Refractometry

Aim and Relevance

- Aim

to close the knowledge gap between solutions and dispersions in refractometry.

- Relevance

the possibility of a new particle sizing and microstructure determination technique by the advent of automatic refractometers.



An old Abbe refractometer



A new digital refractometer



Colloidal Refractometry

Refractive index of mixtures: solutions & dispersions.

- Refractive index of a pure sample, n .
- Refractive index of a mixture or a clear solution as a function of the solute volume concentration, ϕ , solute refractive index n_p , and solvent or continuous phase's refractive index n_c can be written as:

$$n = n_c + \phi(n_p - n_c)$$

- What would be the refractive index of a dispersion or an emulsion in terms of the dispersed phase properties?
- How would the particle size feature in that expression?

$$n = n_c + \phi(n_p - n_c)f(d_{x,y})$$



Colloidal Refractometry

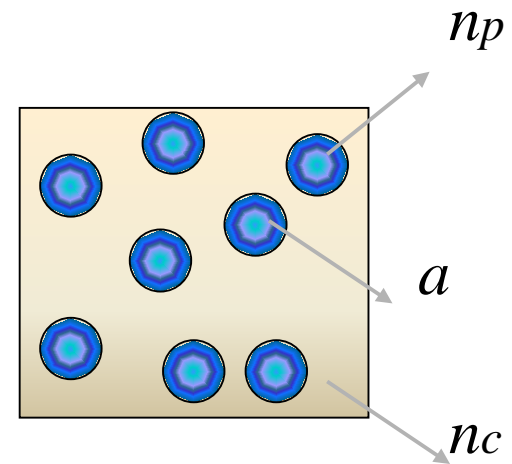
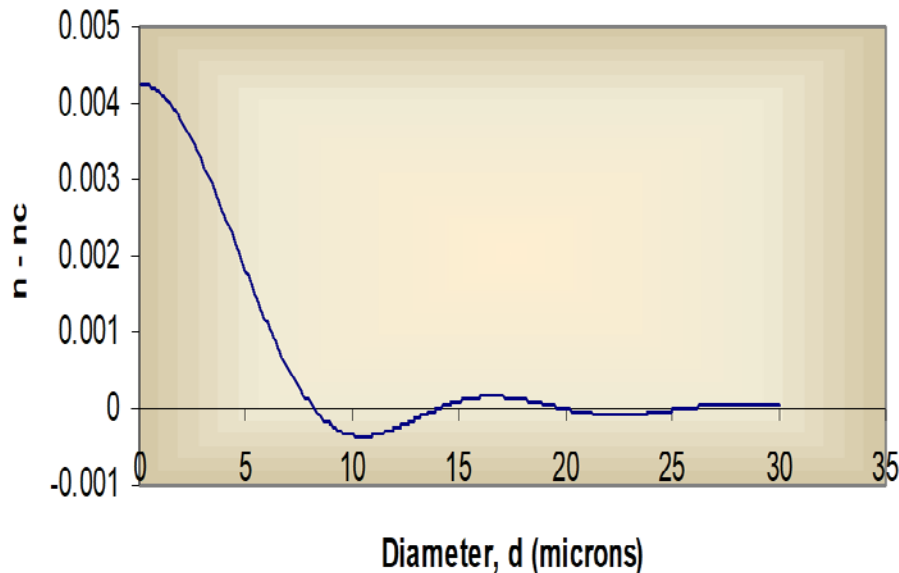
The generalised refractive index equation:

The anomalous diffraction approximation to Mie

$$n = n_c + \phi(n_p - n_c) \left(\frac{3 \sin p}{p^3} - \frac{3 \cos p}{p^2} \right)$$

$$p = 4\pi a(n_p - n_c) / \lambda_0$$

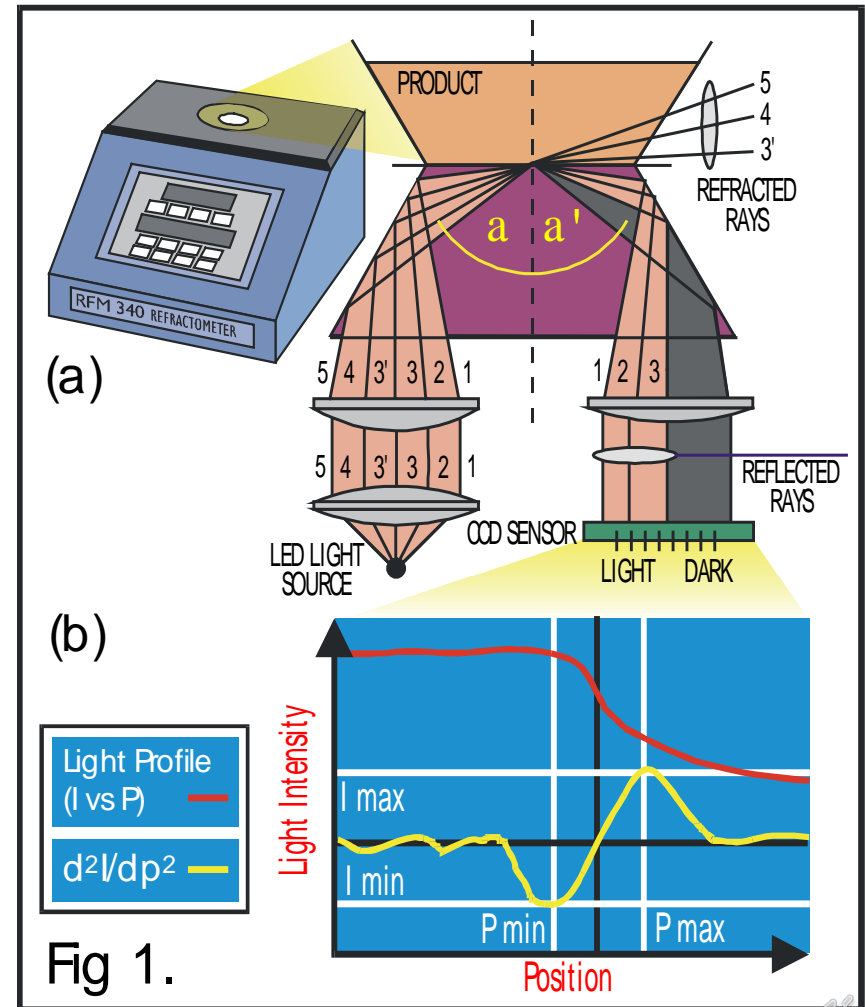
Refractive index of a dispersion v particle size
according to the Anomalous Diffraction expression



Colloidal Refractometry

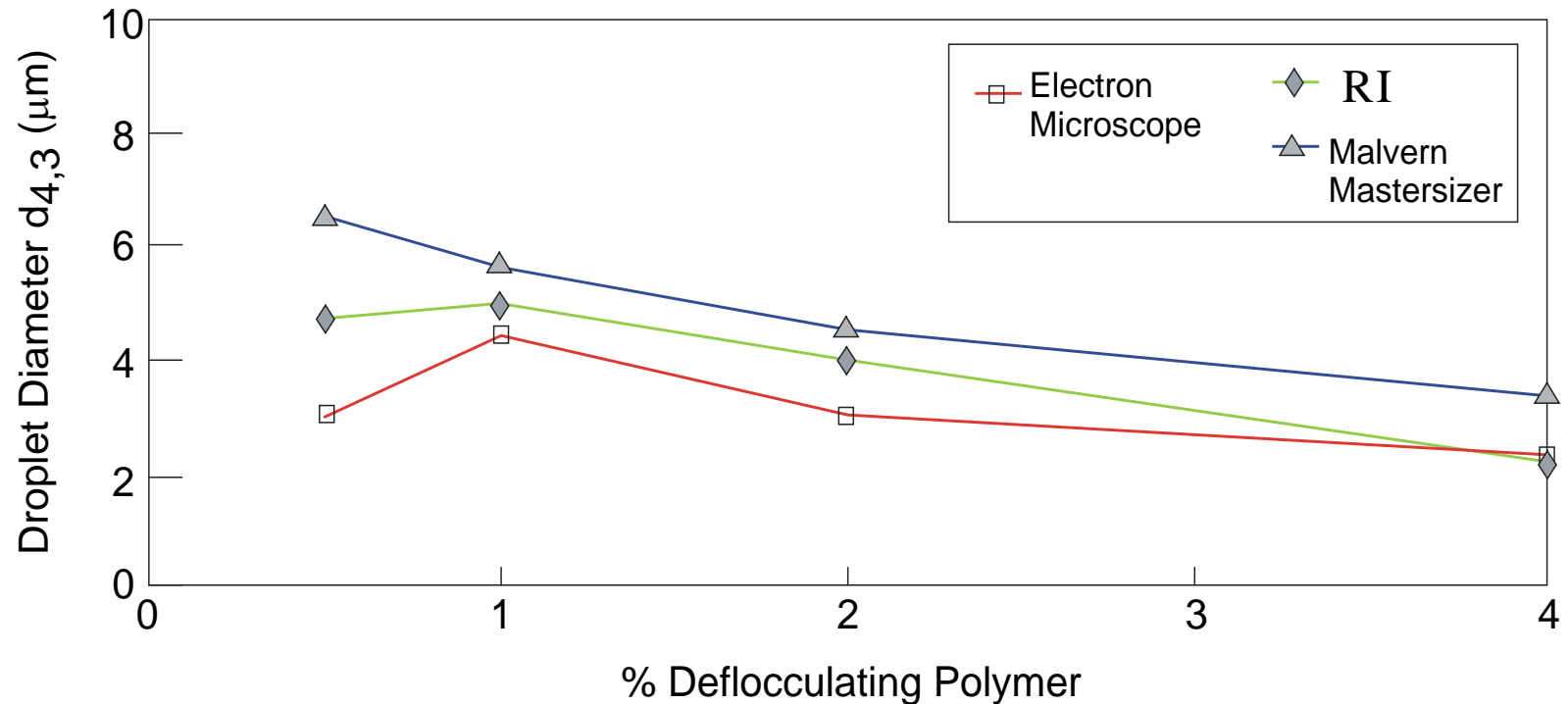
Automatic critical-angle refractometers

- Position of a sharp light-dark demarcation for transparent liquids gives the value of n ,
- Turbid dispersions give a diffused edge - gradual change rather than discontinuous,
- Differentiating the light intensity v position once or twice pinpoints the cut-off edge - hence n readout accurate to $\pm 2 \times 10^{-5}$,
- One or two drops of a neat liquid suffices to give a refractive index reading.
- We used a Bellingham-Stanley RFM340 for the measurements here.



Colloidal Refractometry

Measuring L_α liposome de-flocculation in a surfactant system (liquid detergent)



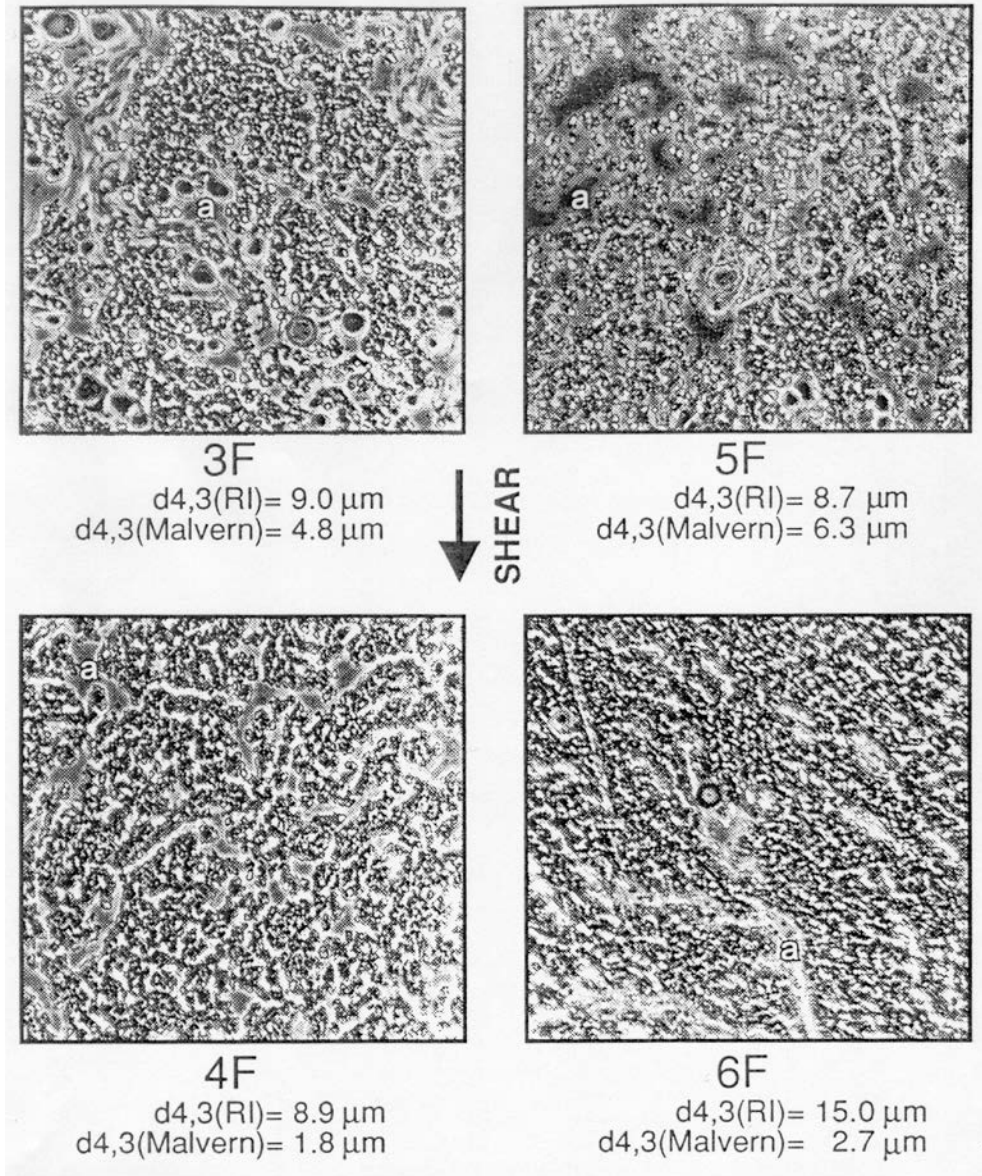
- The generalised refractive index (RI) equation appears to give the volume-surface average size, $d_{4,3}$, rather than other averages.



Colloidal Refractometry

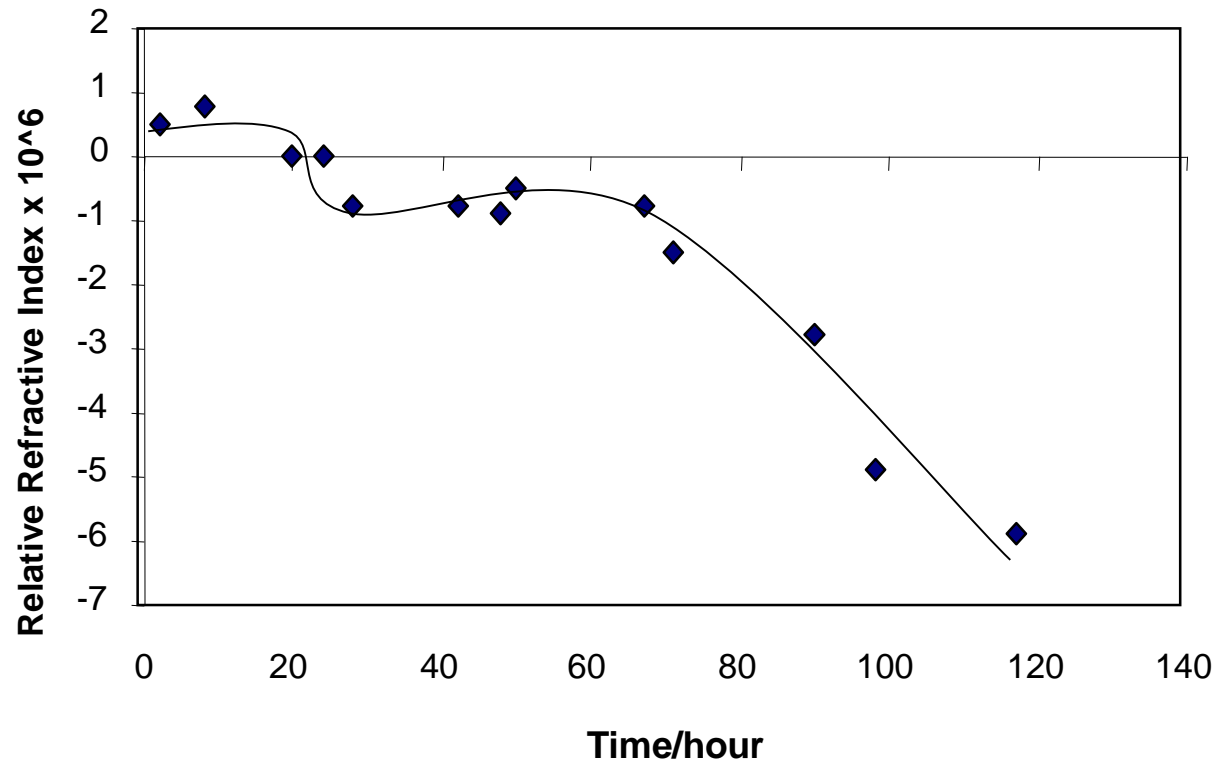
Primary v floc size in liposome dispersions

- Shear induced flocculation widens the discrepancy between the two methods, the Malvern Mastersizer and refractive index(RI).
- The sizes from RI agreed with the rheology and creaming behaviours of the dispersions.



Colloidal Refractometry

Measuring flocculation in polymer latices

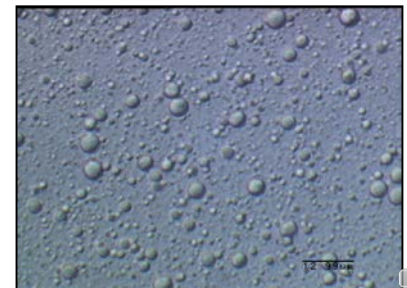
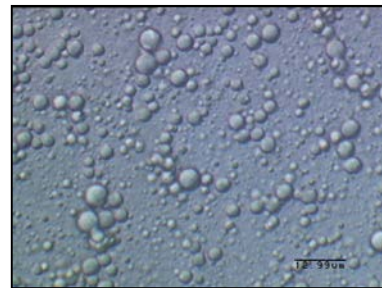
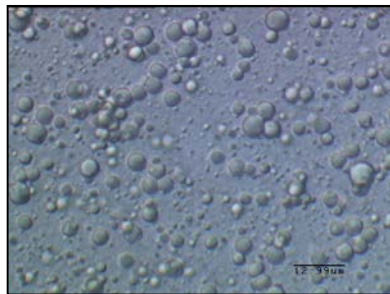
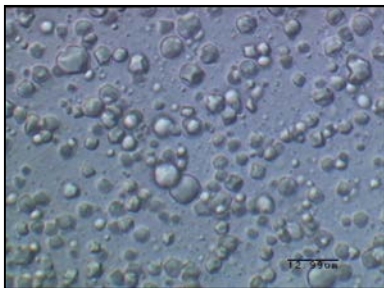
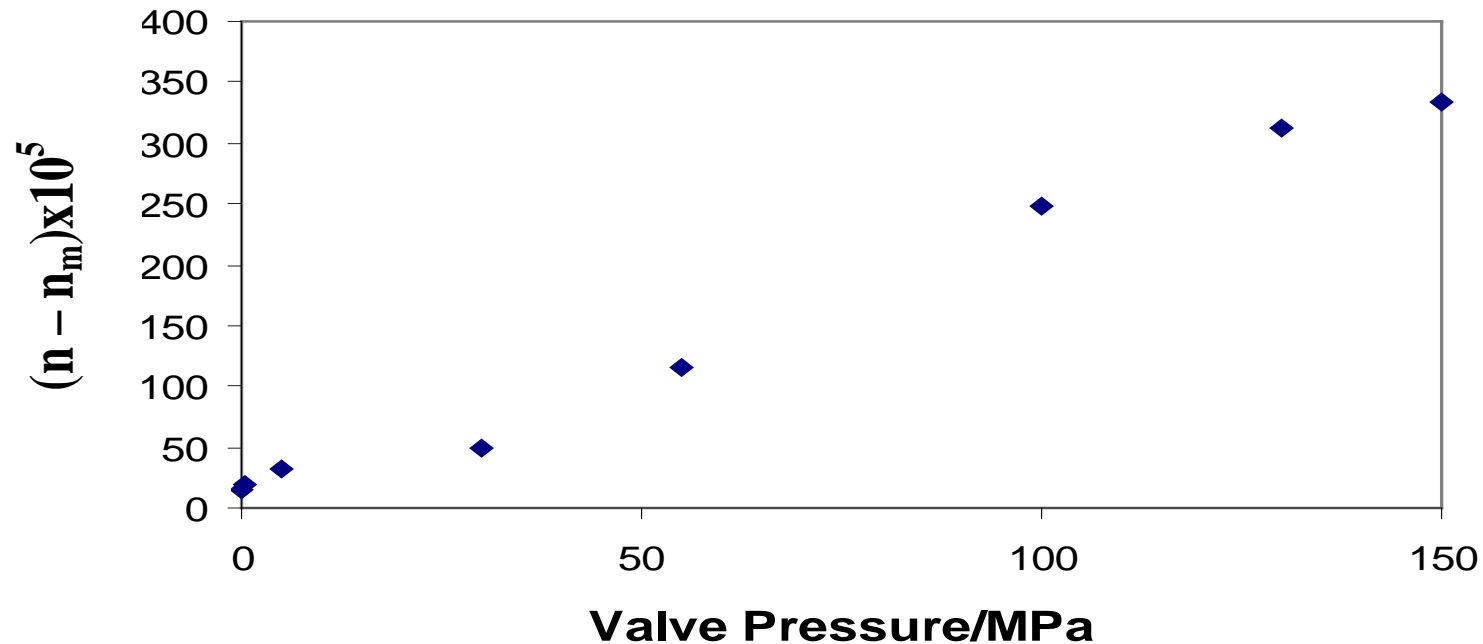


- The change in the refractive index of a polyvinyltoluene latex with time during the slow aggregation by addition of NaCl.



Colloidal Refractometry

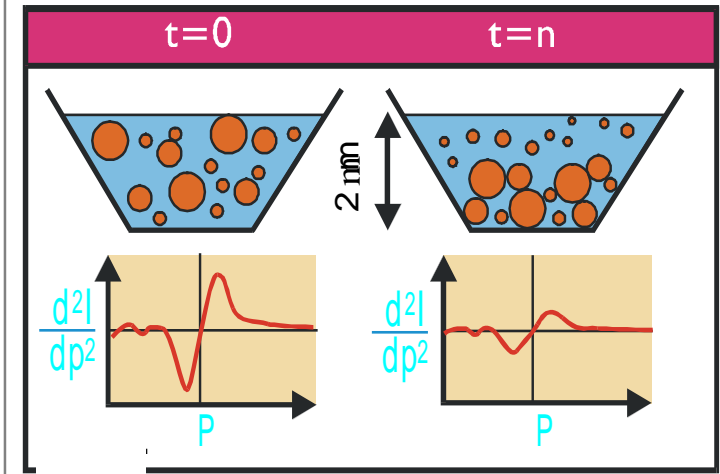
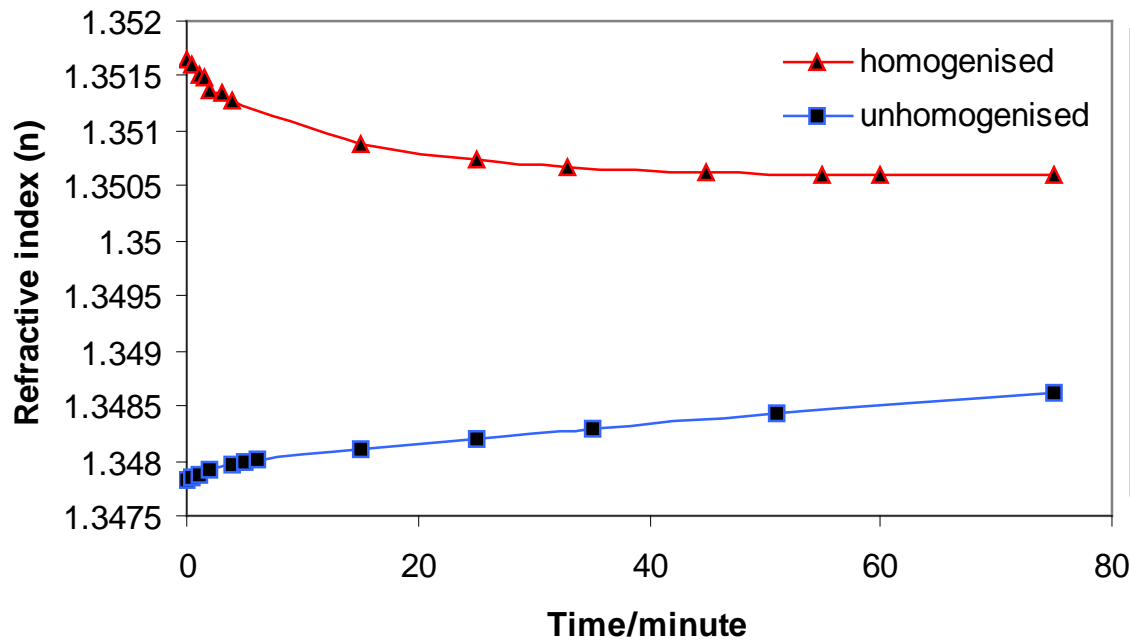
Increase in refractive index with homogenisation of full-fat milk as fat globules become smaller



Colloidal Refractometry

Fast forecasting of creaming/sedimentation

- Kinetics of creaming for two full-fat milk samples studied by measuring the change in refractive index with time.



- A few drops of the sample remains on the sampling space of the prism where light penetrates only a few micron deep and records particle movement and change in concentration in a micrometre size space. To see such changes macroscopically will need days.



Colloidal Refractometry

Acknowledgement and References

- Unilever Research Port Sunlight for permission to present the work.
- Dr. Gerry Meeten (Schlumberger Research Cambridge) for guidance and advice,
- Mohammadi M S, Colloidal Refractometry, The Art of Microstructure Characterisation, Chapter 7 in 'Particle Sizing and Characterisation', volume 881 in the ACS Symposium Series, 2004'.
- This reference gives the historic perspective, background theory and application of the new method with full references to the original work.

