Application of LF-NMR Relaxation to Determine the Hansen Solubility Parameter (HSP) of Polymerics and Colloidal Particles

David Fairhurst, PhD., Colloid Consultants, Ltd.
Ravi Sharma, PhD., Mageleka Inc.

UK Colloids (2021)
Colloids in Energy
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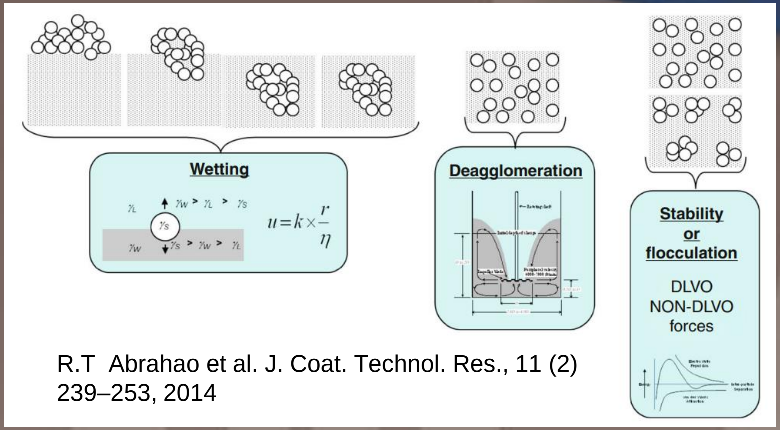
Particle Dispersions are important in the development of many commodity products

- Coatings, inks, pharmaceuticals and cosmetics etc., increasingly employ micro- or nano-particles carefully formulated in a variety of carrier fluids

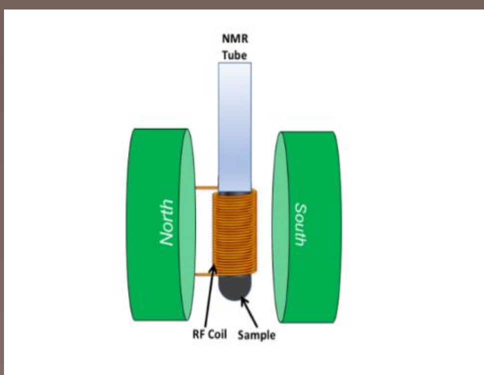


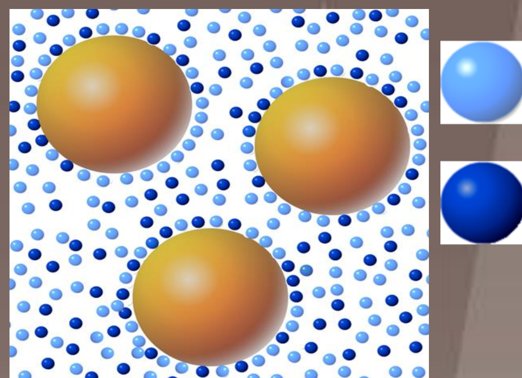
R.T Abrahao et al. J. Coat. Technol. Res., 11 (2) 239–253, 2014

- Dispersing a powder into a liquid phase is a critical process step in formulating and manufacturing
- A predictive method for selecting appropriate solvent or solvent mixture in wetting and dispersion of powders has practical and economic benefits
- **Hansen Solubility Parameter** (HSP) method suggested as a useful approach to predict solvent quality for wetting of powders

NMR solvent relaxation……

Solvent molecules in contact with an interface are not free to rotate and translate as in the bulk. Hence the relaxation times are shorter.





liquid molecule that was free

liquid molecule that was bound

Observe a single relaxation that is a weighted average

$$R_{av} = R_f (1-\varphi) + R_b \varphi$$

φ = proportion of bound liquid

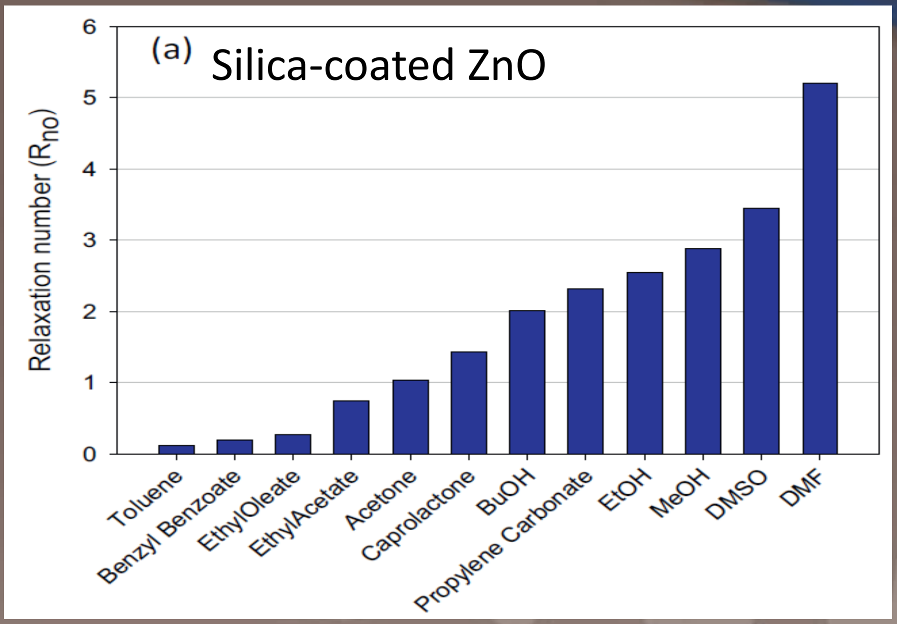
R_b = relaxation rate of bound liquid

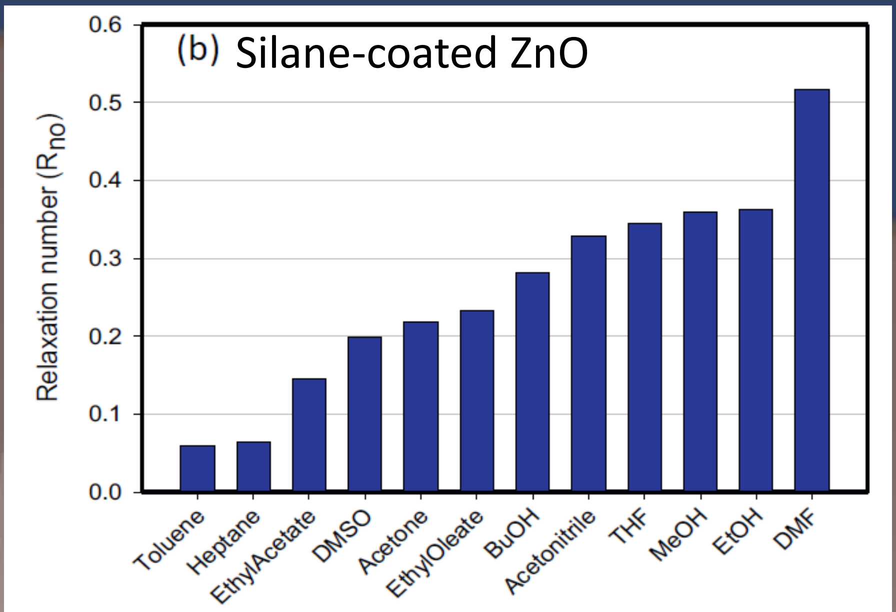
R_f = relaxation rate of free liquid

Relaxation rate, R = 1/Relaxation time, T

…….can rank order compatibility of solvents with powders…..

Relative Relaxation Rate, $R_{no} = (R_{susp} - R_{solv})/R_{solv}$

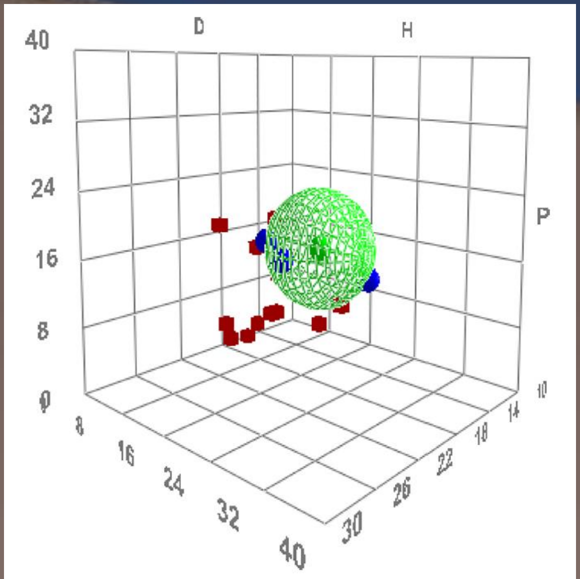


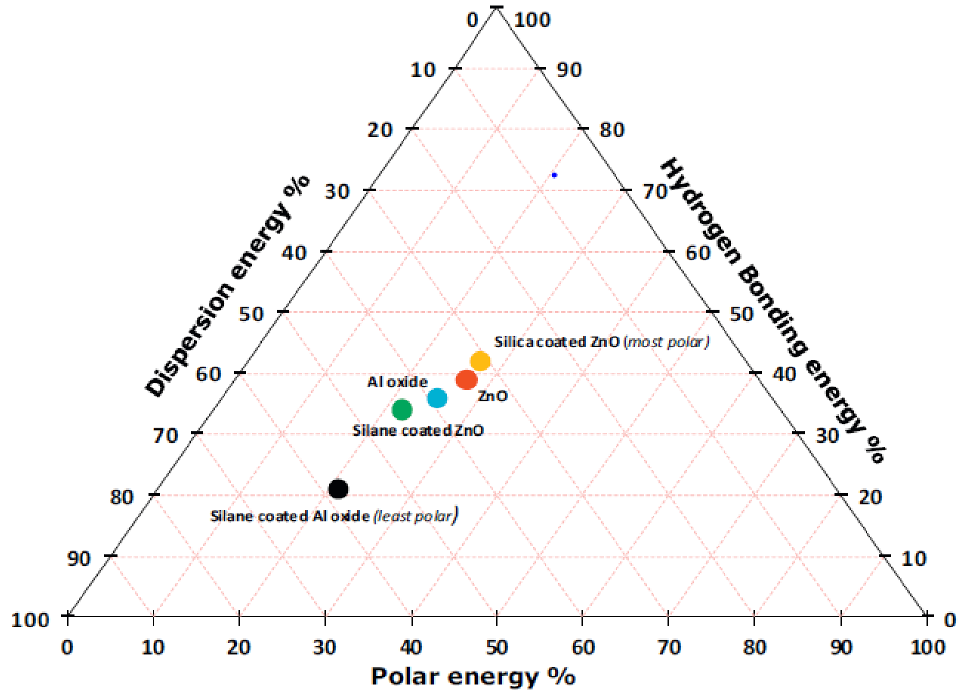


Larger R_{no} value → increased surface-solvent interaction → more efficient wetting

R_{no}, for two nanosize Zinc Oxide powders are significantly different → predicts particle stability

….and determine the HSP of particles…..

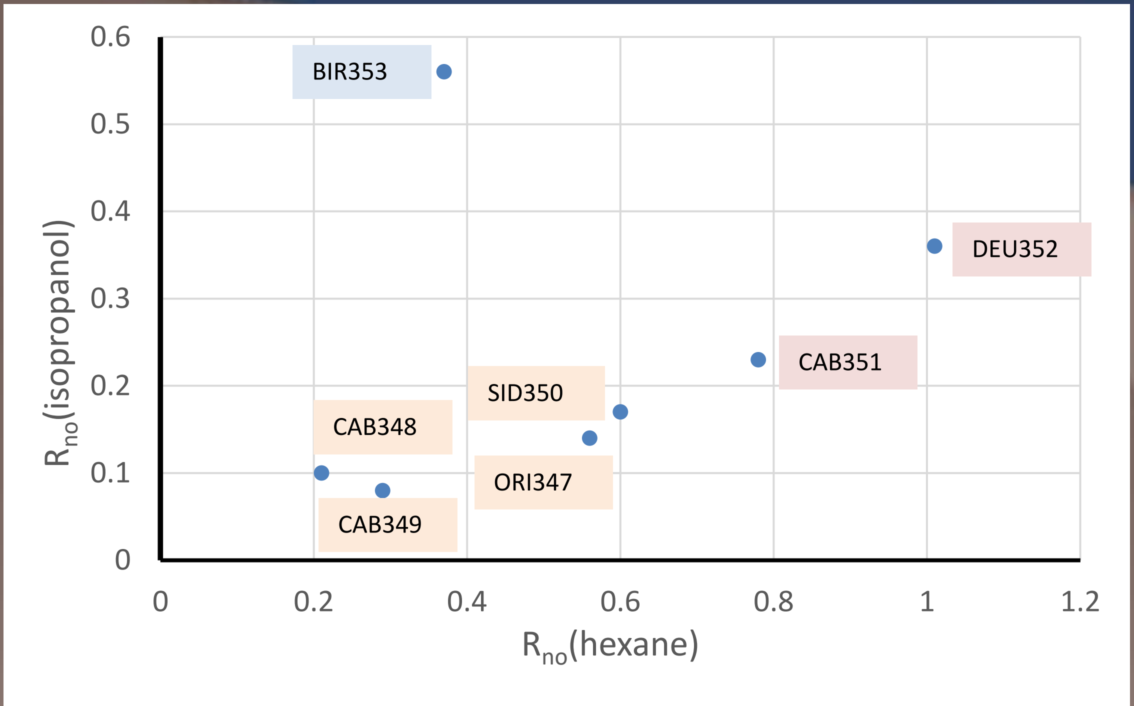




D.Fairhurst, R.Sharma *et al*,
Powder Technology, 377 (2021) 545-552

- Large difference in HSP for silica-coated ZnO *cf* silane-coated ZnO
- Uncoated ZnO and Al_2O_3 have similar HSP
- Silane-coated ZnO and Al_2O_3 have significantly different HSP → surface coatings cannot be the same

Surface properties of Carbon Blacks



The NMR results cluster into three "areas of HSP space" in which reside different groupings of the seven Carbon Black materials

The 353 BIRLA material is clearly atypical compared with all the other carbon blacks

HSP for hexane: D=14.9, P=0, H=0; HSP for IPA: D=15.8, P=6.1, H=16.4)

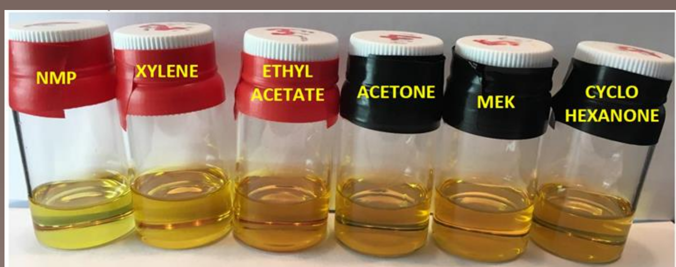
Hexane-Carbon Black interaction strength arises solely from the Dispersive force

Isopropanol-Carbon Black interaction has large contribution from Hydrogen-bonding

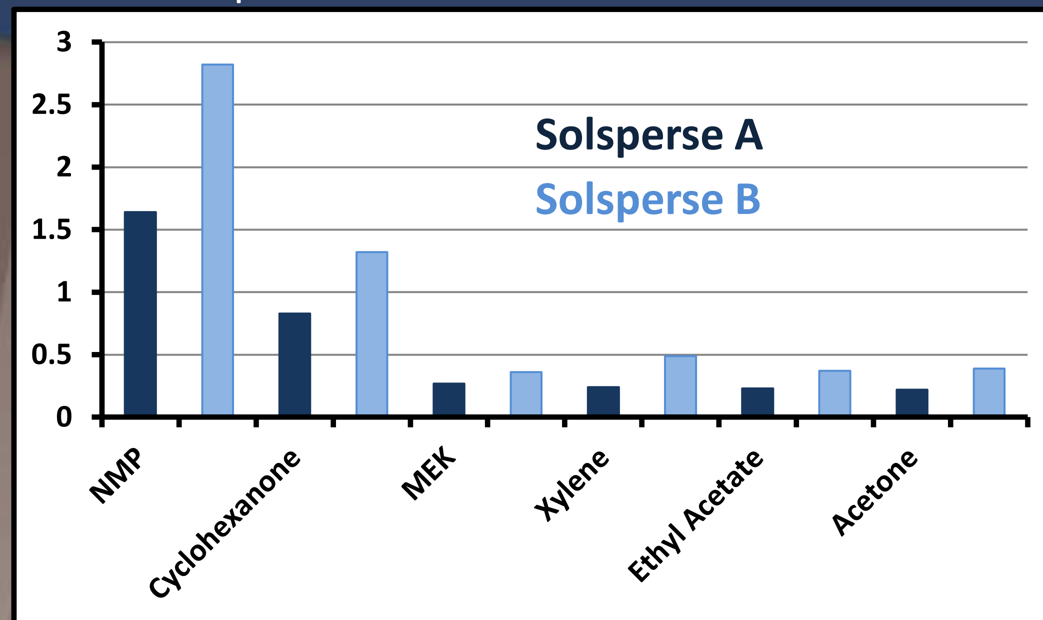
Solubility of Polymeric Dispersants

Solsperse A

Solsperse B



Comparison of Relative Relaxation Rates



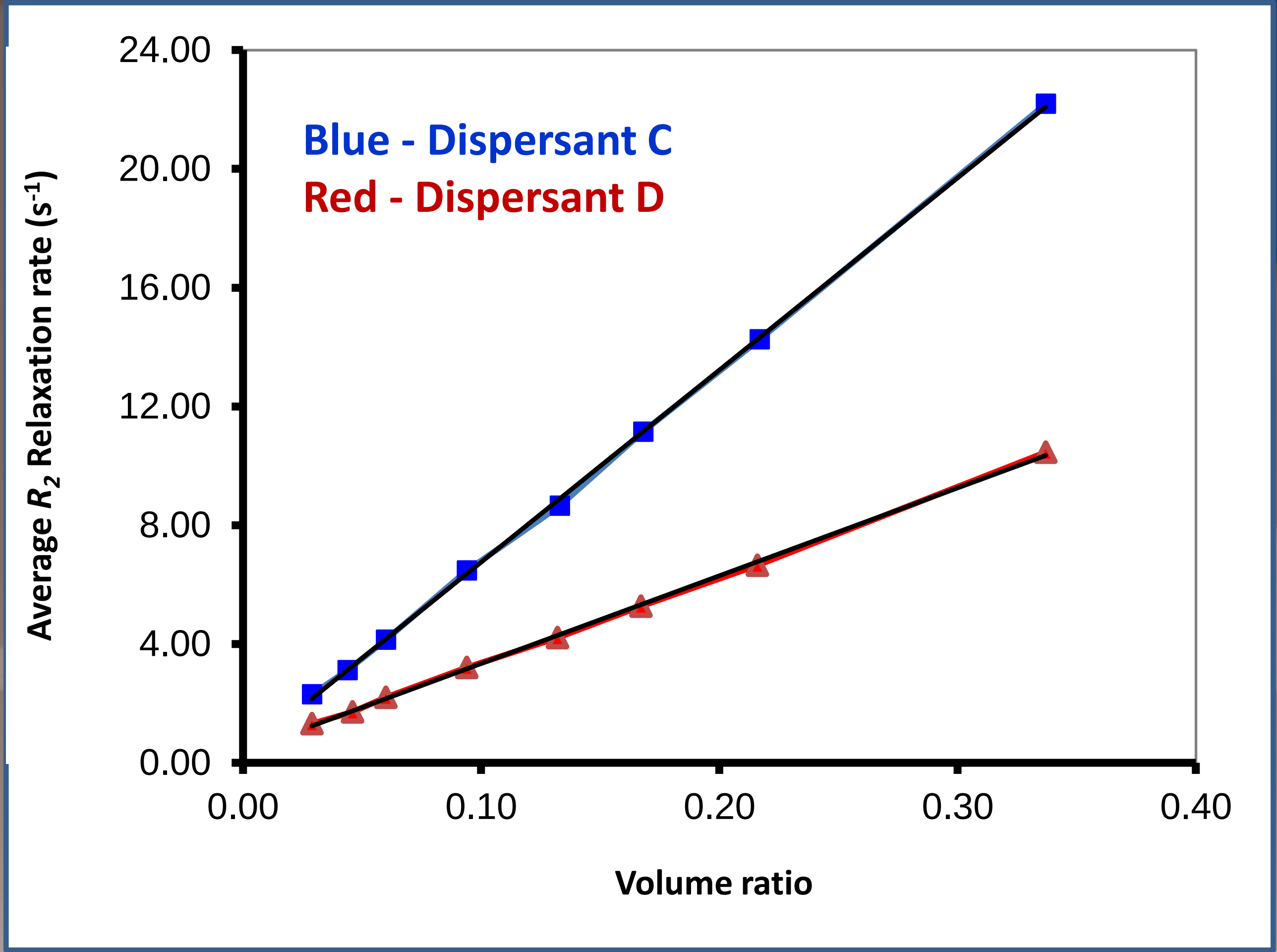
Solution of both hyperdispersants are visually totally clear in all the solvents

Solvent relaxation NMR provides *quantitative* differentiation of compatibility with solvents

Solsperse B is more compatible with the solvents than is Solsperse A

Comparison of dispersant efficacy

Mageleka



Dispersant C is better than Dispersant D

Conclusion

- NMR relaxation is a useful complimentary technique for selecting suitable solvents for:
  (a) wetting and dispersion of powders
  (b) preparation of formulations utilizing polymeric dispersants

- Low Field NMR relaxation measurements can:
  - provide a relatively fast and simple way to characterize solid-liquid interfaces (HSP, dispersion quality), and solvent-additive interactions
  - discriminate between material surface chemistry, and surface chemical coatings
  - offer time-saving information in formulation
  - optimize and select liquid composition for desired particle suspension performances

Thank You!

Email: Ravi@mageleka.com
www.mageleka.com