APPLICATION OF LF-NMR RELAXATION TO DETERMINE THE HANSEN SOLUBILITY PARAMETER (HSP) OF PARTICLES

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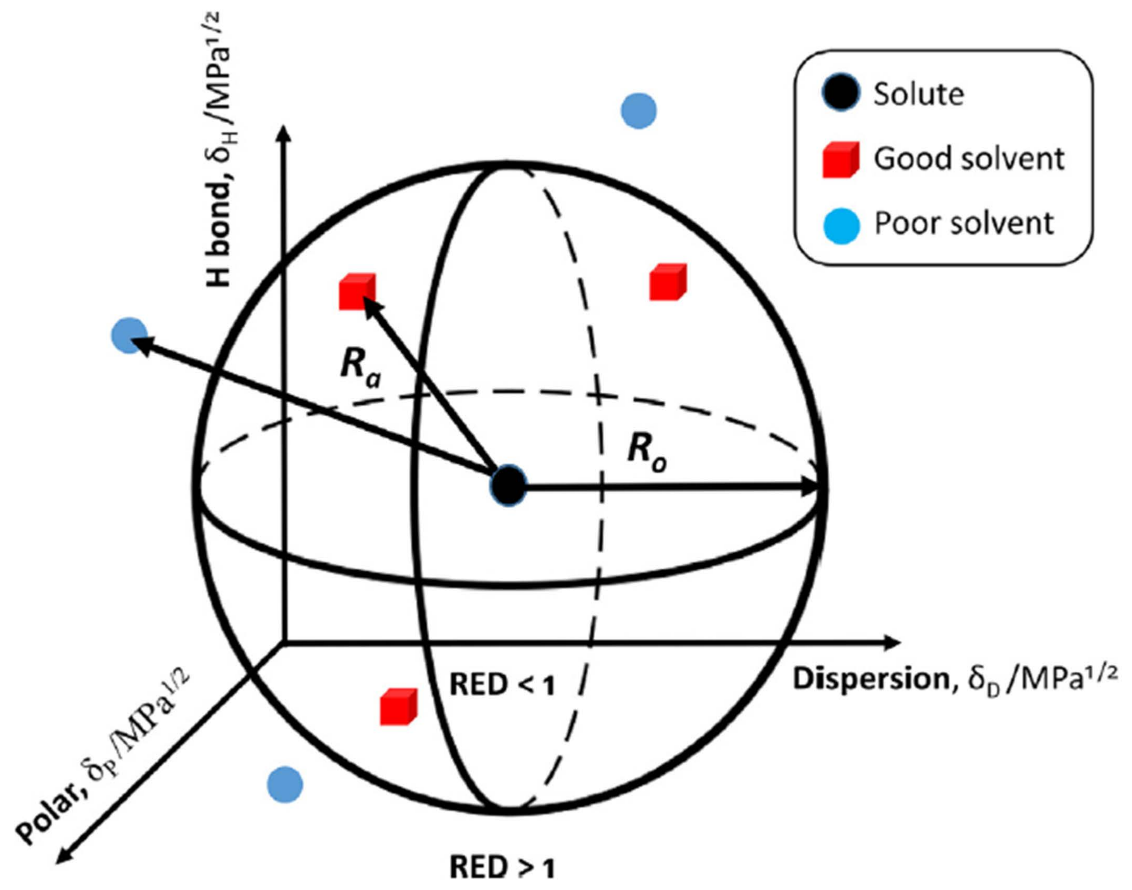
INTRODUCTION

- Achieving particle-solvent compatibility is a key step in the preparation of many products e.g., inks, paints, cosmetics
- Currently sedimentation times are used to rank order solvent compatibility and when used with the Hansen Solubility Parameter (HSP) approach, solvents can be rationally selected based on the HSP value of the particle
- Molecular-level interactions determine solvent suitability but are difficult to measure; existing experimental approaches (mainly sedimentation) require slow/expensive tests of dispersion stability
  - ➢ Time consuming, subject to error, often requires extra step of diluting, can be complicated and need to account for viscosity and density
- Solvent relaxation NMR measurements are shown to be a fast indicator of solvent suitability, with sensitivity to the solvent-particle intermolecular forces making it a reliable proxy for stability measurements.
  - ➢ Time saving, easy to do, no dilution required
  - ➢ Practical and economic benefit
- The application of the approach is illustrated using a range of surface modified zinc oxide and aluminum oxide particles, with similarities and differences between the particle surfaces becoming evident through the analysis.

From Powder

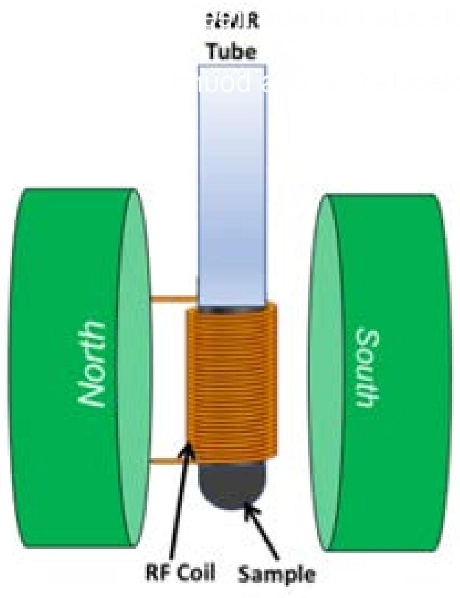
Solvent-particle compatibility is a *key enabler*
It drives key processing steps: wetting, de-agglomeration, stability

To Product

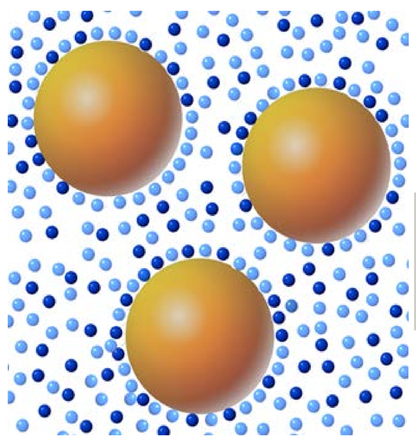


^{1}H NMR RELAXATION

Solvent relaxation NMR can discriminate between highly mobile (liquid-like) and immobile (solid-like) protons on the basis of magnetic relaxation rates.
A high R_{no} indicates good solvent-particle compatibility,
Can rank-order solvent affinity for particle surface



Free liquid molecule- long relaxation time (s)
Bound liquid molecule- short relaxation time (ms)

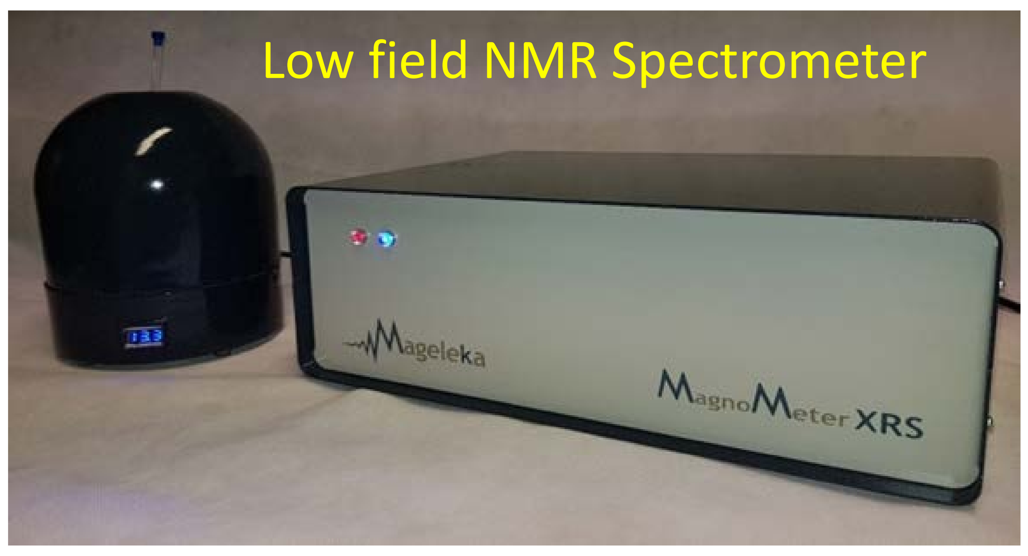


Observe a single relaxation that is a weighted average

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

Φ : proportion of bound liquid
R_b : relaxation rate of bound liquid
R_f : relaxation rate of free liquid

$$R_{no} = [R_{susp}/R_{solv}] - 1$$



PARTICLES

Characteristics of the aluminum oxides.

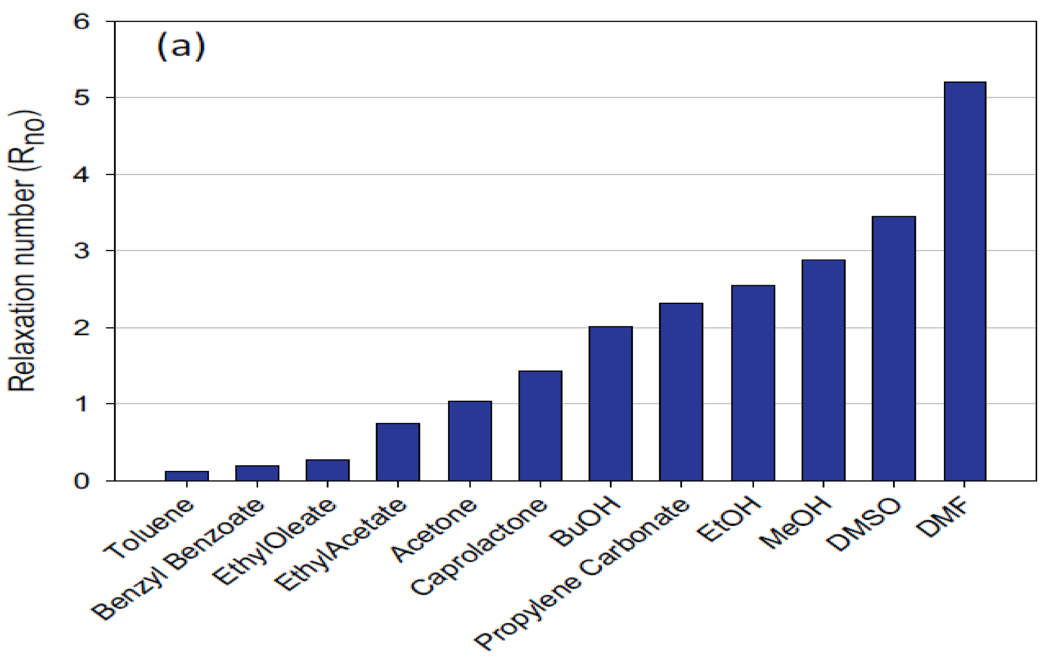
Coating	Surface	Aqueous behavior	ζ potential/mV	Mean particle size/nm
None	Hydrophilic	Cationic	+45	ca 300
Silane	Hydrophobic	Non-wettable	N/A	ca 300

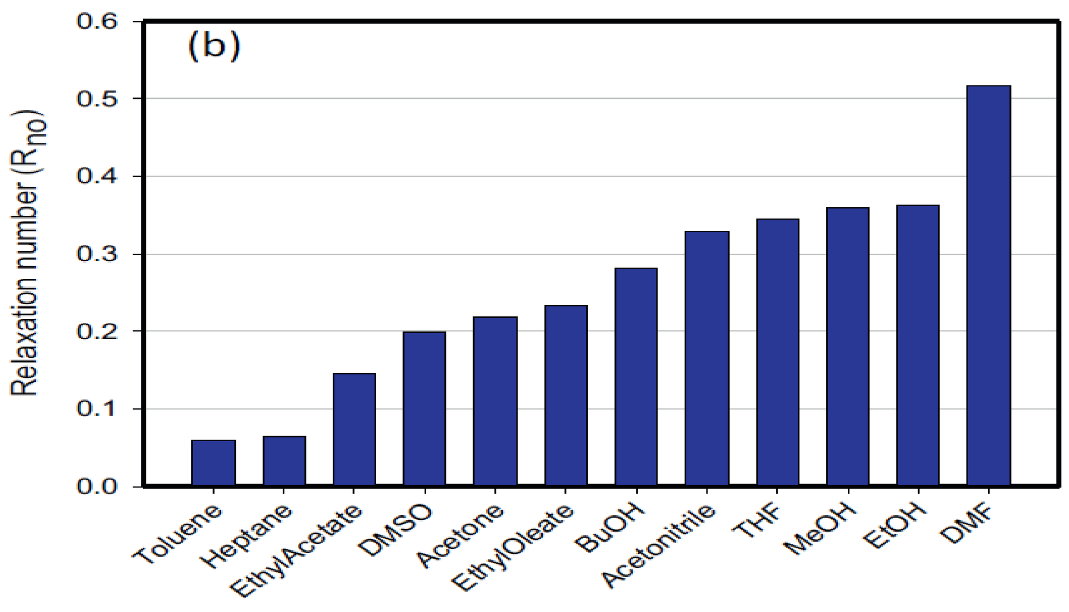
Characteristics of the zinc oxides.

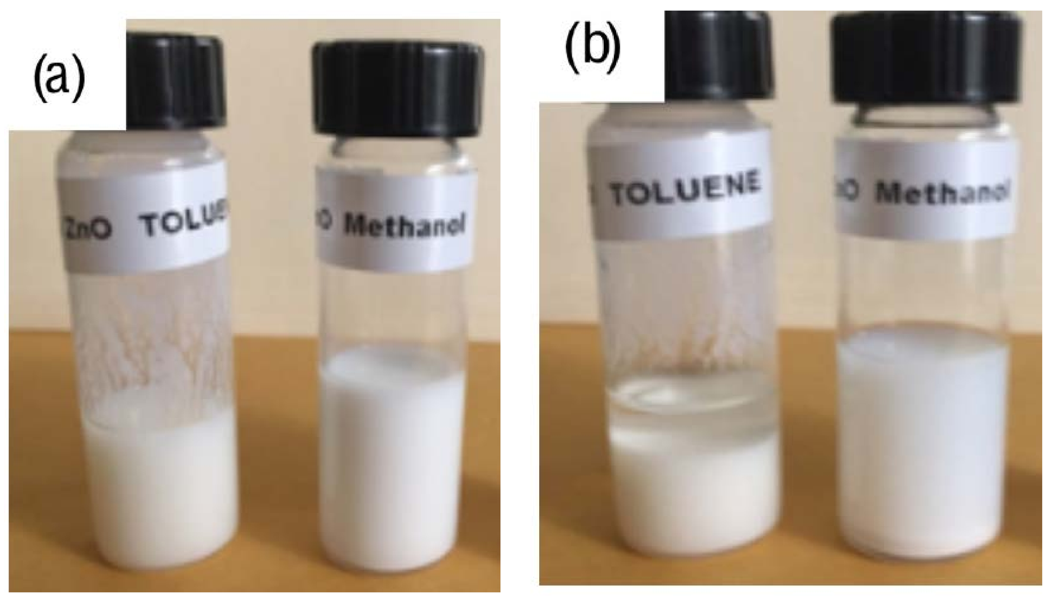
Coating	Surface	Aqueous behavior	ζ potential/mV	Z_{avg} particle size/nm
None	Hydrophilic	Cationic	+39	122
SiO_2	Hydrophilic	Anionic	−55	159
Silane	Hydrophobic	Non-wettable	N/A	138

RESULTS - NMR RELAXATION

Comparison of the Relaxation Numbers (R_{no}) for zinc oxide powders in a variety of solvents, showing the different solvent affinity between (a) silica-coated and (b) silane-coated powders.







Dispersions of silica-coated zinc oxide in toluene, methanol (a) immediately after preparation, (b) four hours later. The separation and flocculation of the dispersion in toluene can be seen in the photographs and is predicted by the very low Relaxation Number.

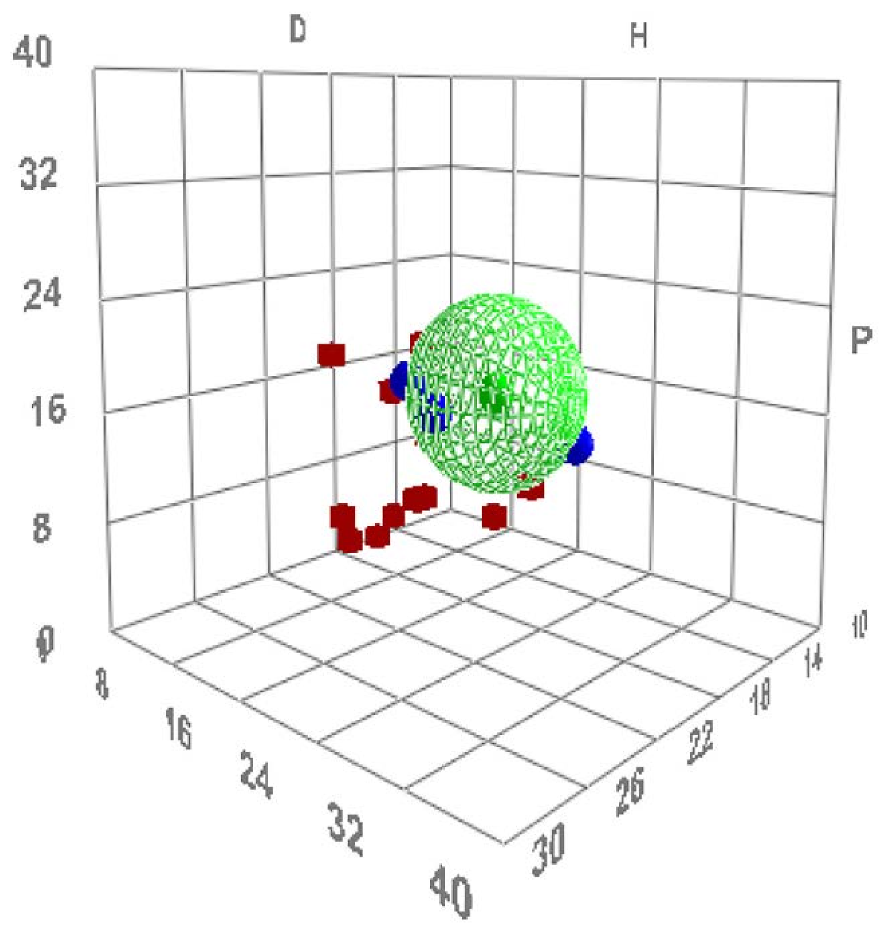
RESULTS - HSP ANALYSIS USING ^{1}H NMR SOLVENT RELAXATION DATA

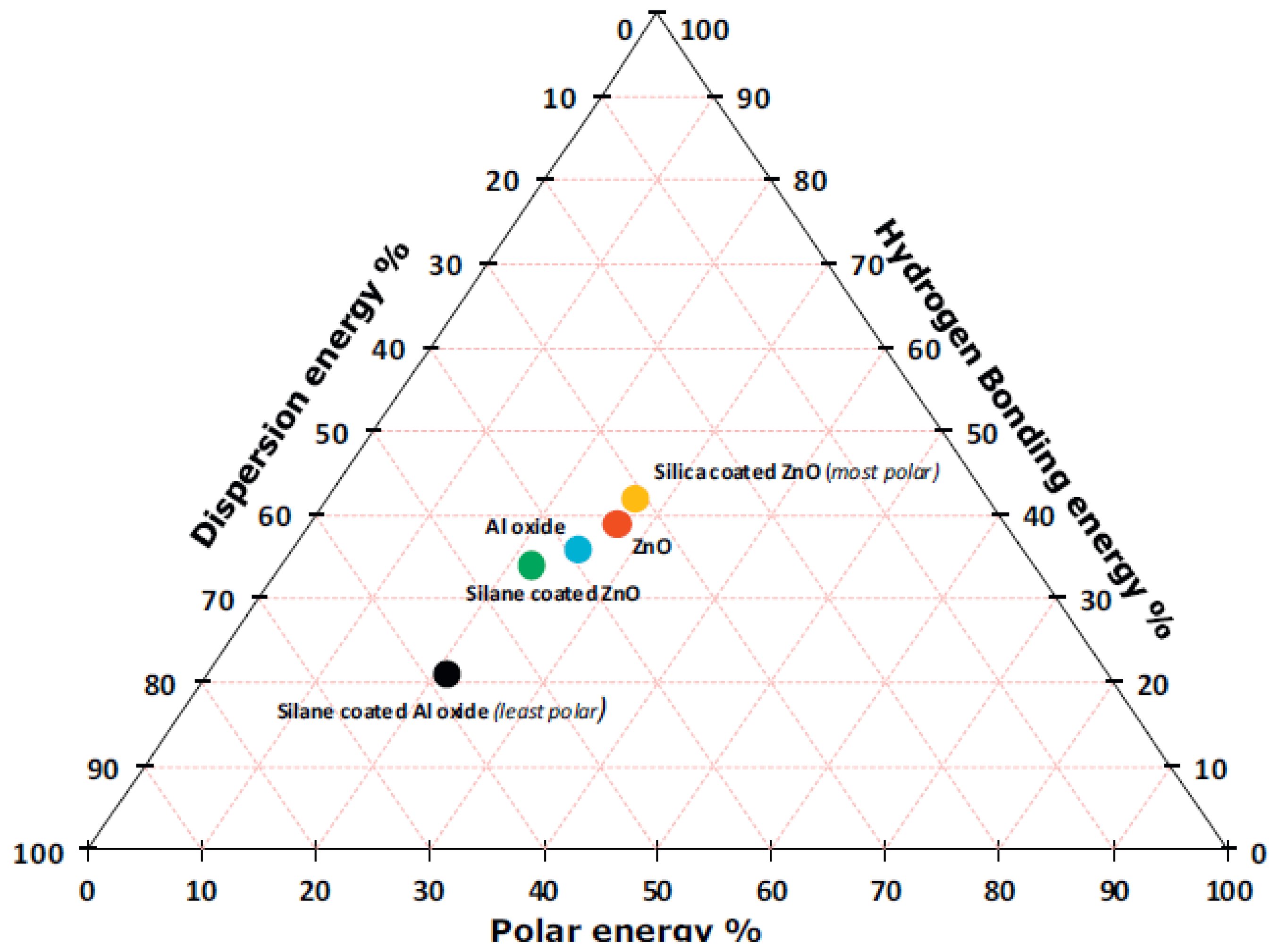
The Relaxation Numbers were used to derive a boundary between good and poor solvents within HSP space. The HSP for this silica-coated zinc oxide material were obtained from the sphere: Dispersion, δD =16.58 MPa$^{1/2}$, Polar, δP = 14.82 MPa$^{1/2}$ and Hydrogen Bonding, δH = 22.11 MPa$^{1/2}$

Table 4
HSP parameters derived for the zinc oxides and aluminum oxide powders[a].

Material	Coating	Surface	δ_D MPa$^{1/2}$	δ_P MPa$^{1/2}$	δ_H MPa$^{1/2}$
Zinc oxide	None	Hydrophilic	15.95 (35%)	12.18 (27%)	17.64 (39%)
	SiO_2	Hydrophilic	16.58 (31%)	14.82 (27%)	22.11 (42%)
	Silane	Hydrophobic	18.51 (45%)	8.97 (22%)	14.05 (34%)
Alumina	None	Hydrophilic	18.03 (36%)	12.52 (25%)	19.50 (39%)
	Silane	Hydrophobic	17.97 (58%)	6.40 (21%)	6.59 (21%)

[a] Values in parentheses are the percentages of each interaction energy shown in Fig. 4.



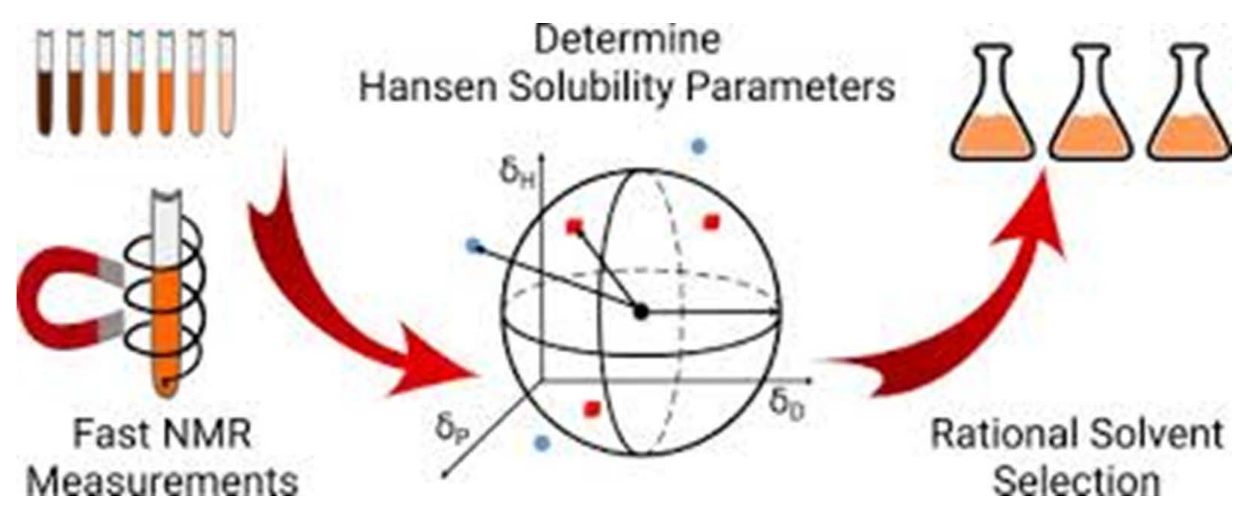


Teas plots for all five oxide powders based on the HSP results. The progression from the most polar particles (silica-coated ZnO) to the most hydrophobic particles (silane-coated aluminum oxide) is clearly demonstrated

CONCLUSION

The initial Relaxation Number is a good index of the propensity of a suspension to settle and so can provide the formulator with useful information.

- Gives the formulator the option of using the information in short time well before there are any visible signs of change in concentrated suspensions.
- NMR solvent Relaxation Numbers can be used to rank order solvent suitability and to determine the HSP value for the test particle. Provides a rational approach for selecting most suitable solvents/solvent mixtures to disperse the particle.



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