New solvents for agrochemical formulations, and scientific methods for selecting solvents

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INTERNATIONAL CROP-SCIENCE CONFERENCE & EXHIBITION

Organised By PESTICIDES MANUFACTURERS & FORMULATORS ASSOCIATION OF INDIA PMFAI

iFormulate

New solvents for agrochemical formulations, and scientific methods for selecting solvents

- Where are solvents used in Agrochemicals
- Issues with old solvents
- New solvents
- Are EC Formulations Dying Out?
- Selecting Solvents
  - Hansen Solubility Parameters (HSP)

Solvents

- "Old"
- Petroleum Based
- Aromatic
- Xylene
- Solvesso 100, 150 and 200
- NMP
- Isophorone

- "New"
- Natural Vegetable Oils
- Long Chain Aliphatic Carboxylic acids
- Triglyceride esters
- Methylated vegetable oils

Solvesso™ Range

	Distillation Range (IBP) (°C)	Distillation Range, Dry Point (DP) (°C)	Flash Point (°C)
Solvesso™ 100	165	181	50
Solvesso™ 150	180	205	65
Solvesso™ 150 ND	180	193	64
Solvesso™ 200	237	285 (FBP)	105
Solvesso™ 200 ND	247	301 (FBP)	113

Atosol® Range

	Atosol 100	Atosol 115	Atosol 150	Atosol 200	Atosol 200ND
Specific Gravity	0.86 - 0.88	0.86 - 0.88	0.89 – 0.91	0.97-1.01	0.97-1.01
Appearance	Colorless liquid	Colorless liquid	Colorless liquid	Straw colored liquid	Straw colored liquid
Boiling Point Range	149 - 177°C 300 - 350°F	145 to 185°C 293 to 365°F	177 - 224°C 350 - 435°F	217 - 296°C 423 - 565°F	232 - 296°C 450 - 565°F
Flash Point	≥ 40°C ≥ 104°F	≥ 40°C ≥ 104°F	≥ 61°C ≥ 142°F	> 93.3°C > 200°F	> 93.3°C > 200°F
Vapor Pressure @ 20°C	< 5 mm Hg	< 5 mm Hg	< 1mm Hg	< 1mm Hg	< 1mm Hg
Solubility in water	Negligible	Negligible	Negligible	Negligible	Negligible
OSHA Flammability	Combustible Liquid	Combustible Liquid	Combustible Liquid	-	-
DOT Flammability	Combustible Liquid	Combustible Liquid	Combustible Liquid	-	-

Total Petrochemical USA website

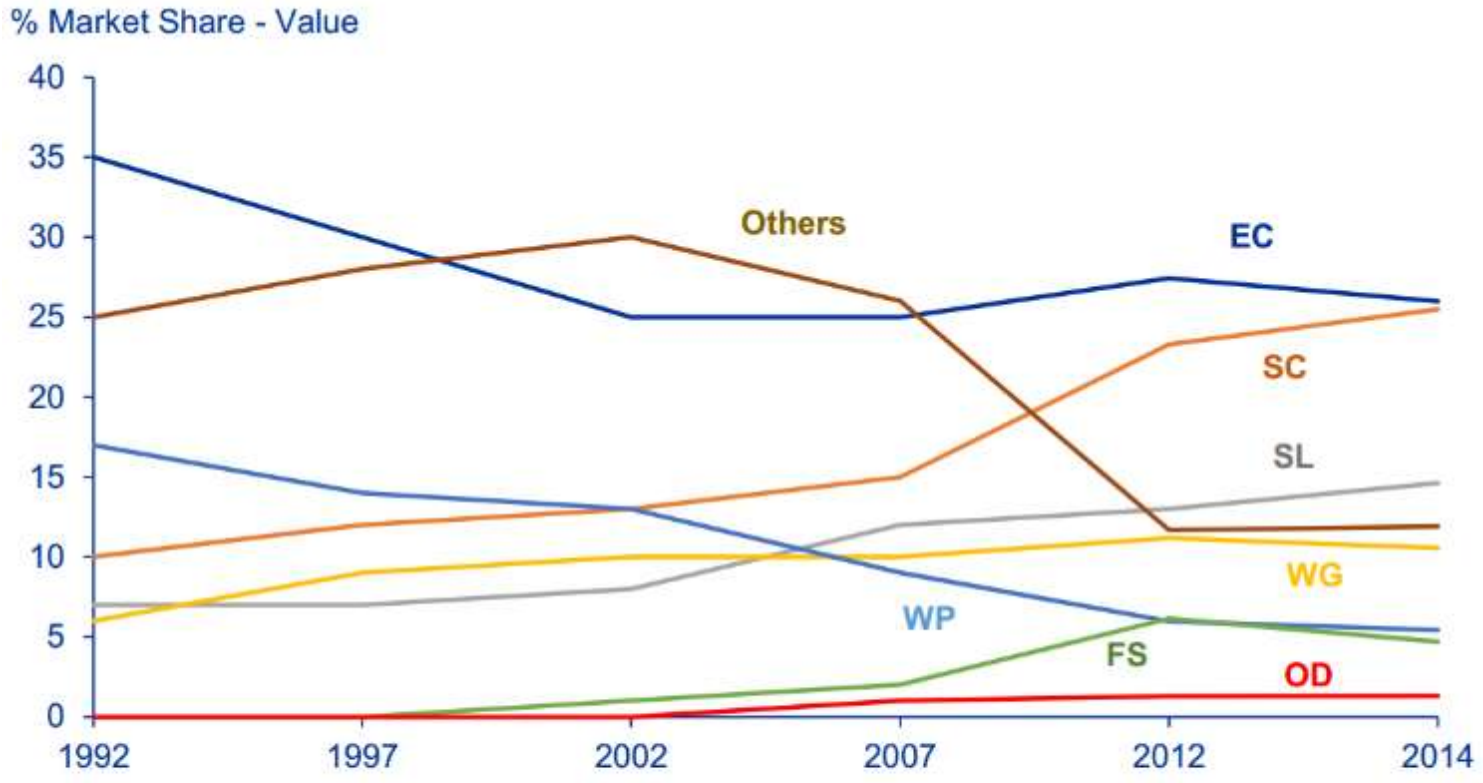
Liquid Formulation Types used for Herbicides	
Formulation Type	Number
EC	159
SC	106
SL	59
OD	9
ULV (UL, SU, EO, OL and OF)	6
EW	6
CS	6
SE	6
ME	4
Liquid	3
Total Liquids	364

Agrow Formulations 2016. J.Bullock/D.Calvert, Informa Agribusiness Intelligence https://store.agra-net.com/awfn16.html. Data is from Pesticide Manual

Fungicide Active Ingredients – Frequency by Formulation Type	
Formulation Type	Number
Liquid Formulations	
EC	79
ULV (UL, SU, EO, OL and OF)	7
SC	120
SL	26
EW	11
CS	1
OD	3
ME	4

Agrow Formulations 2016. J.Bullock/D.Calvert, Informa Agribusiness Intelligence https://store.agra-net.com/awfn16.html. Data is from Pesticide Manual

Formulation Types by Value: Old Data 2014



Key Drivers

SC – Soybean Fungicides and Insecticides/Rynaxypyr/Cereal fungicides
SL – Non-selective herbicides/herbicide tolerant crops
FS – Seed treatment / GM Crops
WP – China (older products), Japan (Jumbo and One-Shot formulations)
WG – Europe cereal herbicides and vines

Source: M.Phillips (Phillips McDougall) at Informa C&C Berlin 2017

Reports of the Death of EC Have Been Exaggerated

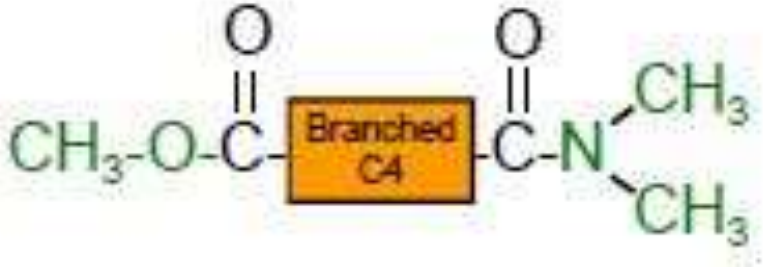
Number of AIs Listed for Main Formulation Types (BCPC Online Pesticide Manual)

Code	Description	No of AIs 2016	No of AIs 2013	Change 2013-2016
EC	Emulsifiable Concentrate	459	339	+35%
WP	Wettable Powder	401	297	+35%
SC	Suspension Concentrate	322	288	+12%
GR	Granule	258	197	+31%
WG	Wettable Granule	196	193	+1.5%
SL	Soluble Liquid	136	113	+20%
DP	Dustable Powder	134	100	+34%
UL	Ultra-low volume (ULV) Liquid	59		
FS	Flowable Concentrate for Seed Treatment	51		
EW	Oil in Water Emulsion	40	38	+5%

Rhodiasolv® IRIS Chemistry#

- Polar and water soluble
- Excellent tox and environmental profiles
- Non-flammable and very low vapour pressure

- Patented Technolgy WO 2009092795
- Being used in commercial pesticides



#http://www.solvay.com/en/markets-and-products/featured-products/rhodiasolv-iris.html

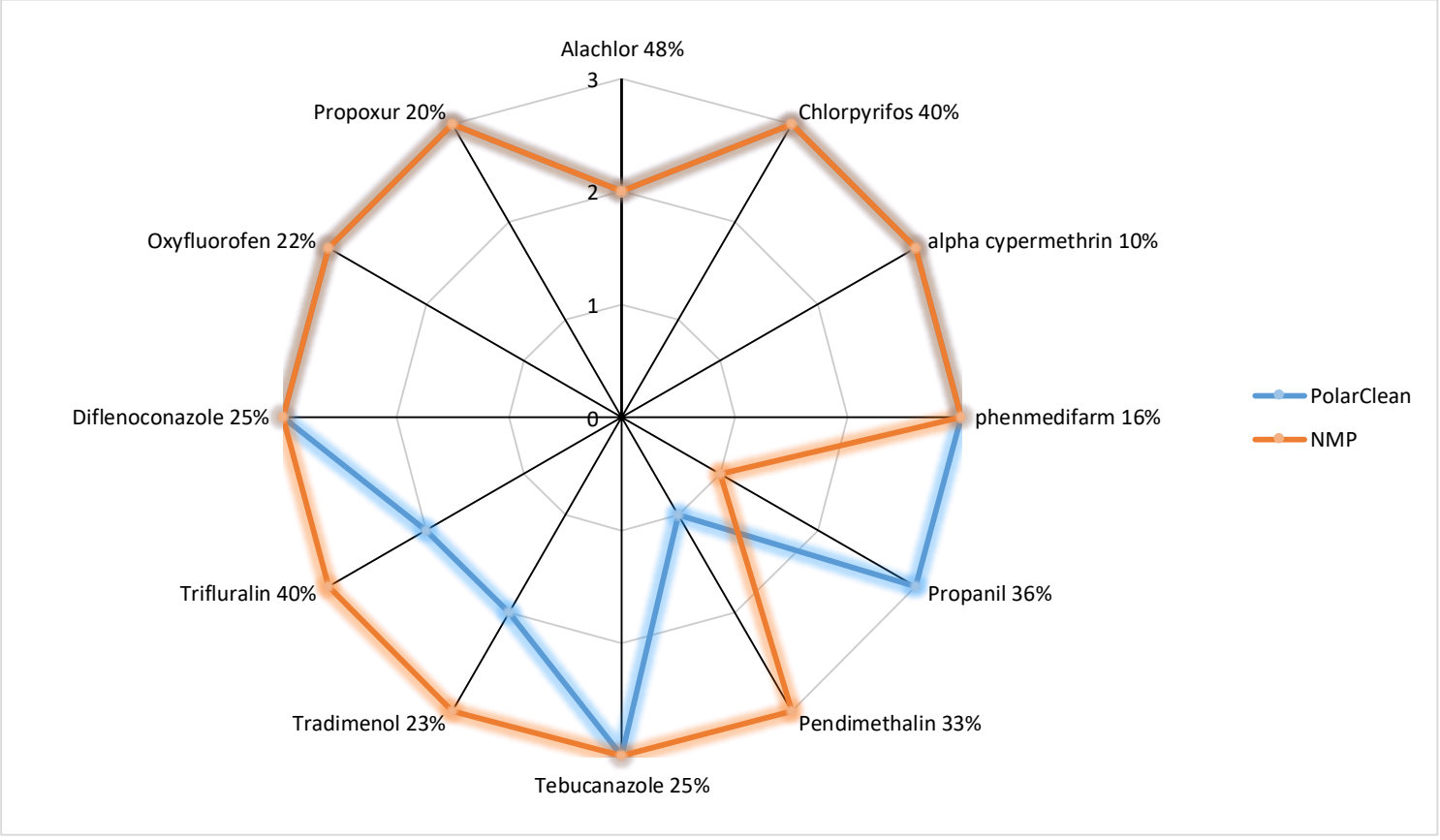
Rhodia* Correspondance 2014 *Now Solvay

Rhodiasolv® IRIS Chemistry

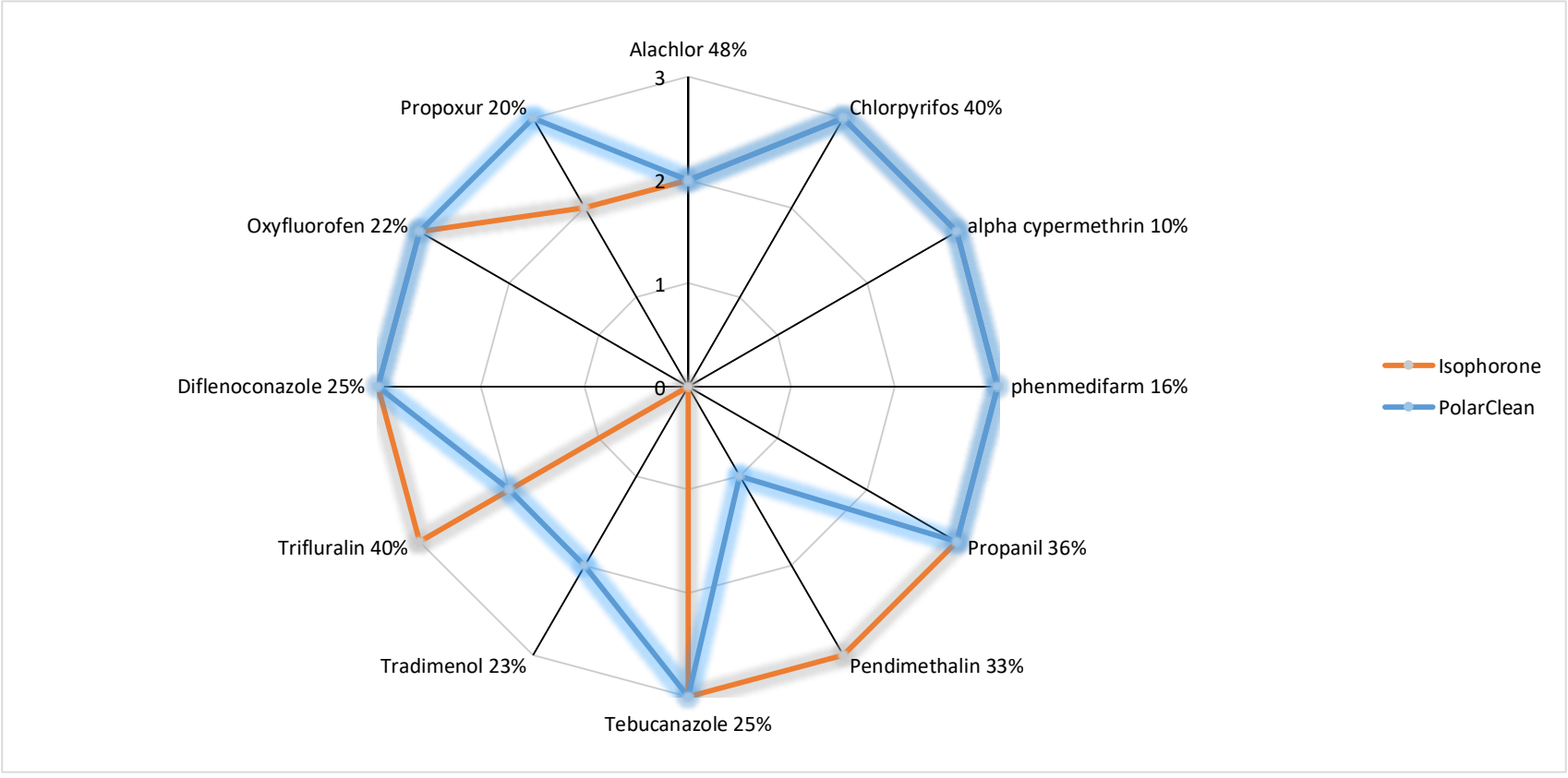
Solvent	Flammability (Flash Point)	Loss on Evaporation	Health and Safety
Rhodiasolv	Non flammable	Very Low	Non toxic Non irritant
Acetone	Flammable	Very High	Flammable
DCM	Non flammable	Very High	Toxic Pot. Carcinogen
NMP	86oC	Low	S2 2009: Reprotox

RSC Symposium 2012 – Not Costing the Earth

RhodiaSolv® PolarClean



RhodiaSolv® PolarClean



Armid FMPC*

- Alternative to N-Methylpyrrolidone
- Water Soluble
- Optimised blend suitable for imidacloprid SLs
  - Up to 200g/l
- Excellent Spray Dilution Stability
  - Low tendency for crystallisation
- Biodegradable

* http://sc.akzonobel.com/en/agriculture/Pages/news-armid-FMPC.aspx

Environmental Profile

Armid FMPC: Environmental profile*	
Acute oral toxicity (rat)	LD50 >5000 mg/kg
Acute dermal toxicity (rabbit)	LD50 >2000 mg/kg
Toxicity to fish	LC50 >500 mg/l Exposure time: 96 h Species: Leuciscus idus (Golden orfe)
Toxicity to daphnia	EC50 >500 mg/l Exposure time: 48 h Species: Daphnia magna (Water flea)
Toxicity to algae	EC50 >100 mg/l Exposure time: 72 h Species: Algae
Biodegradability	>70% DOC, 28 days Readily biodegradable
PBT and vPvB assessment	This substance is not considered to be a PBT (Persistent, Bioaccumulation, Toxic). This substance is not considered to be vPvB (very Persistent nor very Bioaccumulating)

*Literature data

Guide Recipe

Imidacloprid	200g/l
Ethylan 1008	40g/l
Armid FMPC	To 1 litre

Ethylan 1008 enhances dilution properties in water and improves wetting onto the surface

Ex Akzo Nobel Literature

Other Actives

2,4-D acid	47%
Dicamba	>50%
Fenbuconazole	22%
Metconazole	21%
Tebuconazole	25%
Trifloxystrobin	33%

Ex Akzo Nobel Literature

Co-Solvent

Ingredient	Function	Concentration
Trifloxystrobin	fungicide	125 g/l
Witconate P1460 EH + Ethylan NS 500LQ + Ethylan 954 LQ	emulsifier blend	90 g/l
Armid FMPC	co-solvent	200 g/l
Armid DM 10	solvent	q.s. 1 liter

Ingredient	Function	Concentration
Quizalofop-P-ethyl	herbicide	250 g/l
Berol 9968 + Berol 9969	emulsifier blend	80 g/l
Armid FMPC	co-solvent	200 g/l
Solvesso 150 ND	solvent	q.s. 1 liter

Ex Akzo Nobel Literature

Corbion Purasolv*

Solvency

PURASOLV® esters are excellent solvents for many active ingredients and can be used as bio-based and non-toxic replacements for potentially unsafe solvents, such as xylene, toluene, isophorone and N-Methyl-2-pyrrolidone (NMP). PURASOLV esters are perfect for use in pesticide formulations, such as Soluble Concentrates/Liquids (SL), Emulsions in Water (EW), Emulsifiable Concentrates (EC) or Microemulsions (ME). PURASOLV esters can offer multiple functionalities in these formulations including:

- Emulsion solvent (especially PURASOLV® BL and EHL)
- Co-solvent to improve solubility properties of other components (e.g. methylated vegetable oils)
- Co-surfactant/coupling agent for micro-emulsions
- Enhance efficacy of active ingredients

*http://www.corbion.com/biochemicals/chemicals/applications/agro-chemicals

Corbion Products	
PURASOLV® ML	Methyl L-lactate
PURASOLV® EL	Ethyl L-lactate
PURASOLV® NPL	n-Propyl L-lactate
PURASOLV® BL	n-Butyl L-lactate
PURASOLV® EHL	2-Ethylhexyl L-lactate

	PURASOLV ML	PURASOLV EL	PURASOLV NPL	PURASOLV BL	PURASOLV EHL
Herbicides					
desmedipham	-	19	17	16	6
ethofumesate	-	38	37	35	10
Fungicide					
tebuconazole	32	33	32	31	23
propiconazole	84	84	83	83	81
IABC	47	52	48	45	31
imazalil	72	70	68	71	58
Insecticide					
chorpyrifos	64	67	70	66	62
cypermethrin	86	84	85	83	70
endosulfan	31	42	46	48	40
dimethoate	-	70	65	64	49

Table 1. PURASOLV Solubility w/w% (20°C)

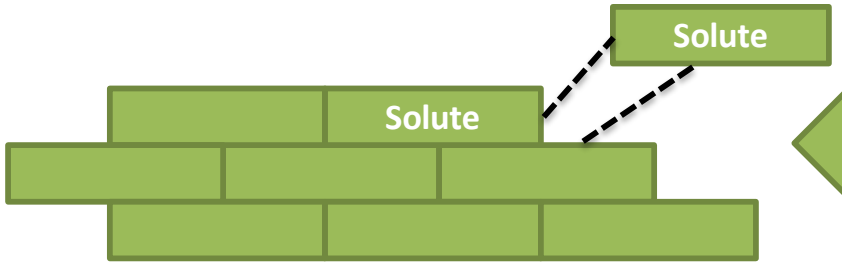
CHOOSING SOLVENTS

Hansen Solubility Parameters: The Basics

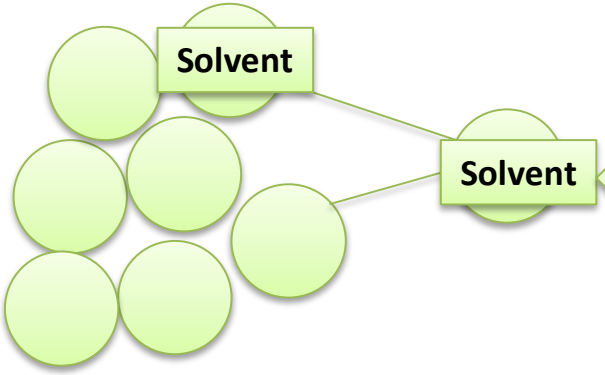
Simply speaking (i.e. without any mathematics)…

- **Solubility is all about interactions (or forces, in some case called bonds):**
  - Interactions between solute and solute molecules
  - Interactions between solvent and solvent molecules
  - Interactions between solvent and solute molecules
- **Thermodynamics tells us:**
  - Pulling molecules apart requires energy
  - Attractive interactions between molecules produce energy
  - Systems tend towards their lowest energy (stable) state
- **Observation tells us:**
  - "Like dissolves like" (e.g. hydrocarbons dissolve other non polar things)
  - But how do we measure "like"?

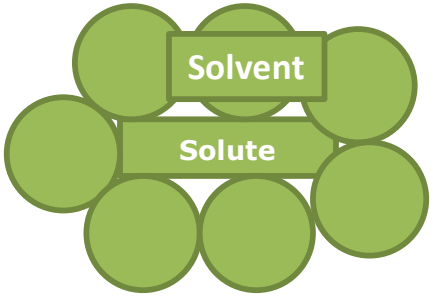
Interactions Between Molecules



Remove solute molecules from the bulk: Doesn't depend on solvent – doesn't really matter when comparing solvents



Break solvent molecules apart: Need to know about forces that have to be overcome



Create interaction between solvent and solute molecules: Need to know about types of interactions created

What Are Those Interactions Anyway?

To cut a long story short, the main things you need to think about are:

Dispersion forces

- Weak intermolecular forces related to polarizability of a molecule and hence to the number of electrons
- Essentially related to the Van der Waals interactions that exist between all molecules

Polar (dipolar) interactions

- Molecules that have a degree of charge separation form an electrical dipole and hence can attract one another electrostatically

Hydrogen bonds

- A special type of polar interaction
- Some atoms on molecules act as donors or acceptors of electrons
- Typically a (partially) positively charged hydrogen atom is attracted to a lone pair of electrons on an electronegative atom (e.g. F, O, N)
- Often seen as “part-way” to a covalent bond

"Like Dissolves Like": How Do We Quantify This?

- Hansen Solubility Parameters quantify the degree of "like" by describing the solvent and the solute using three numbers (HSP)
- You won't be surprised to hear that these numbers relate to the three types of forces we have just heard about:

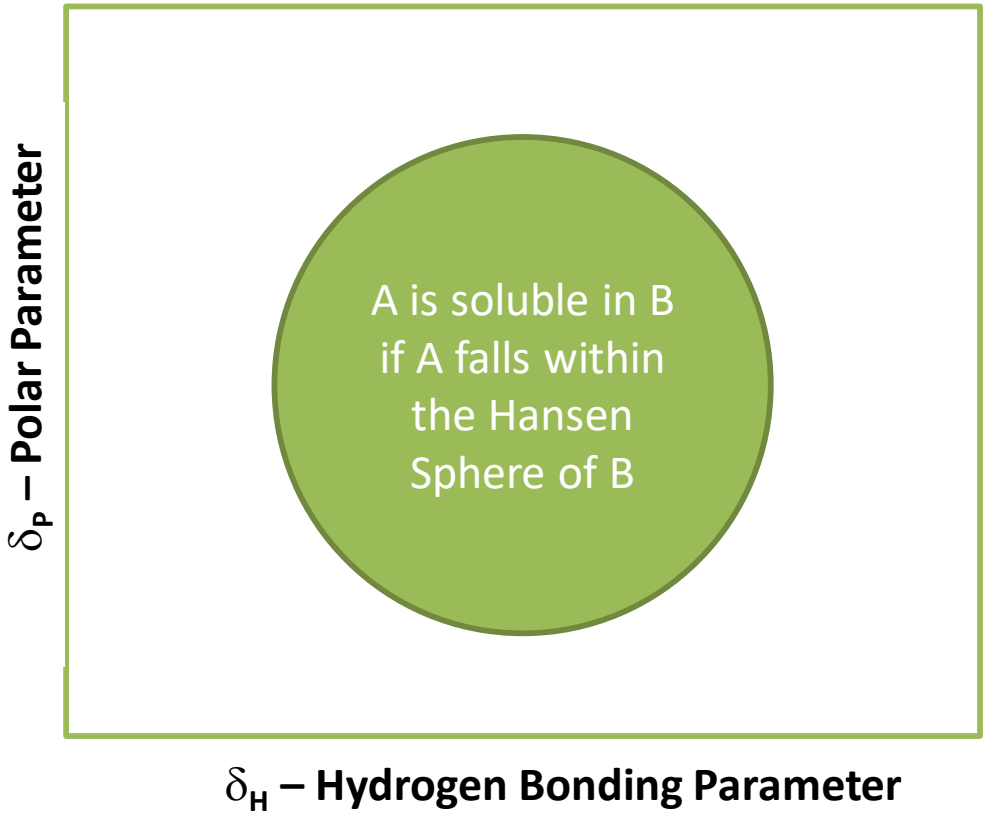
δ_D – Measure of dispersion forces

δ_P - Measure of polar (dipolar) interactions

δ_H – Measure of hydrogen bonding

- The closer the HSP values of solvent and solute, the better the solvent is for that solute
- The "distance" of solvent from solute needs to take into account all three parameters (dimensions):
- $\text{Distance}^2 = 4(\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2$

“Like Dissolves Like” and The Hansen Sphere



In real examples the above circle is a sphere and the third dimension is δ_D the Dispersion Parameter

Two components will be mutually soluble (“in the sphere”) when their parameters are close together, i.e. if the HSP Distance is small

$$\text{Distance}^2 = 4(\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2$$

An Aside: How Is This Related To Thermodynamics and Energy?

E (cohesive energy, = ΔE_{vap}) = $E_D + E_P + E_H$

D - Dispersion (Hydrocarbon)

P - Polar (Dipolar)

H - Hydrogen Bonds (Electron Interchange)

We can normalise the energy to V (Molar Volume), so:

$E/V = E_D/V + E_P/V + E_H/V$, i.e.:

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$$

HANSEN SOLUBILITY PARAMETERS (HSP)

δ = Square Root of Cohesive Energy Density

- Charles Hansen: "Hansen Solubility Parameters: A User's Handbook", Second Edition published 2007, CRC Press.
- Charles Hansen: Doctoral Thesis, 1967.

HSP for PolarClean

	δ_D	δ_P	δ_H
PolarClean	15.8	10.7	9.2
NMP	18	12.3	7.2
Isophorone	16.6	8.2	7.4
ADMA	16.5	6.4	7.3

Corbion PURASOLV
Use of Hansen Solubility Parameters

http://www.corbion.com/biochemicals/chemicals/applications/agro-chemicals

Physical properties	MW	Density	Flsh Point	Viscosity	Vapor Pressure	Evaporation Rate	Surface Tension	Hildebrand $(J/cm^3)^{1/2}$	Hansen Solubility Parameters $(J/cm^3)^{1/2}$			olubility n water	Solubility of water	Particion Coefficient
	g/mol	g/m (20ºC)	ºC/ºF	mPa.s (20ºC)	mbar (20ºC)	n-BuAc=1	mN/m (25ºC)	δ	δ_d	δ_p	δ_h	w/w% (20ºC)	w/w% (20ºC)	log (octanol/ water)
PURASOLV ML	104	1.092	58/136	3.1	3.4	0.26	34.2	23.3	16.3	9.1	13.7	miscible	miscible	-0.50
PURASOLV EL	118	1.033	59/138	2.8	2.2	0.22	30.6	21.7	16.0	7.5	12.5	miscible	miscible	0.03
PURASOLV NPL	132	1.005	69/156	3.3	1.0	0.05	30.4	20.6	15.9	6.9	11.2	miscible	miscible	0.55
PURASOLV BL	146	0.984	79/174	3.9	0.4	0.03	29.5	19.9	15.8	6.5	10.2	4.5	13.9	1.08
PURASOLV EHL	202	0.939	113/235	7.7	0.0	0.00	29.8	18.4	15.7	4.5	8.5	0.03	3.5	3.12

Conclusions

- Environmental pressures do drive formulation development
- BUT
- Must perform
- New solvents for EC formulations have desirable tox and environmental profiles
- AND
- Perform
- HSP a good tool for solvent selection
- EC formulations here for a while to come