# Substitute Green Solvents for the Production of Polymeric Membranes


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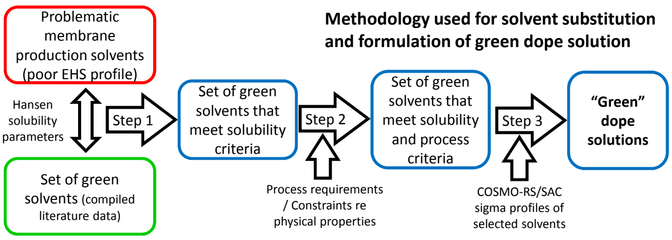
## ❑ The need for change

Environmental, Health and Safety (EHS) concerns associated with typical membrane production solvents and their placement under restrictive regulations are the driving forces behind the search for adequate alternatives also known as "green solvents"

**Problematic solvents widely used in membrane manufacturing**

| Solvent | Hansen solubility parameters, (MPa$^{1/2}$) $\delta_d$ | $\delta_p$ | $\delta_h$ | Boiling point bp (°C) |
|---|---|---|---|---|
| Chloroform | 17.8 | 3.1 | 5.7 | 61 |
| Dichloromethane | 18.2 | 6.3 | 6.1 | 40 |
| Dioxane | 19 | 1.8 | 7.4 | 101 |
| Hexamethylphosphoramide (HMPA) | 18.5 | 8.6 | 11.3 | 255 |
| N,N-dimethylacetamide (DMAc) | 16.8 | 11.5 | 10.2 | 165 |
| N,N-dimethylformamide (DMF) | 17.4 | 13.7 | 11.3 | 153 |
| N-Methyl-2-pyrrolidone (NMP) | 18 | 12.3 | 7.2 | 202 |
| Trichloroethylene (TCE) | 18 | 3.1 | 5.3 | 87 |
| Tetrahydrofuran (THF) | 16.8 | 5.7 | 8 | 67 |
| Dibutyl phthalate (DBP) | 17.8 | 8.6 | 4.1 | 340 |
| Dioctyl phthalate (DOP) | 16.6 | 7 | 3.1 | 384 |
| Toluene | 18 | 1.4 | 2 | 111 |

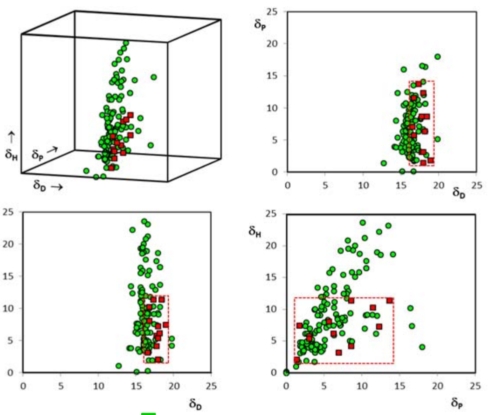
**Methodology used for solvent substitution and formulation of green dope solution**




## ❑ Step 1 – Meet solubility criteria

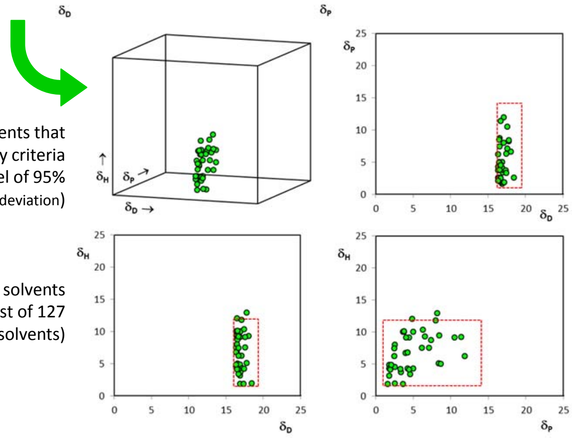
Approach based on the minimization of the modified difference - Ra -between the HSPs of the problematic solvent (1) and the potential substitute (2):

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



Typically, problematic solvents used in membrane manufacture (red squares) occupy a limited section of the "Hansen solubility space"

The compilation of green solvents (127 solvents: green dots) is more evenly spread through the "Hansen space"



Set of green solvents that meet the solubility criteria with confidence level of 95% (mean ± 2 × standard deviation)

40 solvents (32% of the initial list of 127 green solvents)

## ❑ Step 2 – Minimize process / physical properties changes

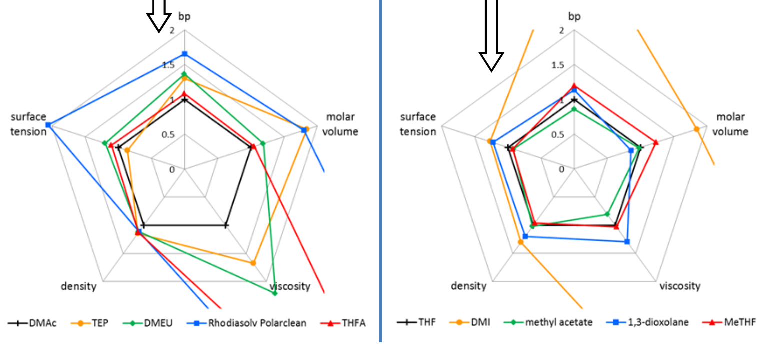
Physical properties of the solvent such as boiling point, molar volume, water miscibility, viscosity, density and surface tension can affect the membrane production process and must also be considered in the evaluation process

__Case study__: **polymeric dope solutions containing DMAc and THF used for dry-wet spinning of polysulfone hollow fibre membranes**

DMAc → ?
THF → ?

| | bp (°C) | molar volume [cm$^3$/mol] | viscosity [mPa.s] | density [g/cm$^3$] | surface tension [mN/m] | "Hansen" distance Ra, [(MPa)$^{1/2}$] |
|---|---|---|---|---|---|---|
| N,N-Dimethylacetamide (DMAc) | 165 | 92.5 | 0.93 | 0.933 | 33.53 | - |
| Triethylphosphate (TEP) | 215 | 170.6 | 1.56 | 1.068 | 28.98 | 1.02 |
| N,N'-Dimethylethyleneurea (DMEU) | 225 | 109.8 | 2.06 | 1.040 | 40.1 | 2.18 |
| methyl 5-(dimethylamino)-5-oxopentanoate (Rhodiasolv Polarclean) | 273 | 166.7 | 9.78 | 1.039 | 69.00 | 3.16 |
| tetrahydrofurfuryl alcohol (THFA) | 178 | 97.3 | 5.35 | 1.050 | 37 | 4.71 |

| | bp (°C) | molar volume [cm$^3$/mol] | viscosity [mPa.s] | density [g/cm$^3$] | surface tension [mN/m] | "Hansen" distance Ra, [(MPa)$^{1/2}$] |
|---|---|---|---|---|---|---|
| tetrahydrofuran (THF) | 67 | 81.7 | 0.46 | 0.882 | 26.5 | - |
| dimethyl isosorbide (DMI) | 236 | 151.2 | 5 | 1.150 | 33.7 | 2.18 |
| methyl acetate | 57.5 | 79.7 | 0.37 | 0.898 | 24.41 | 3.03 |
| 1,3-dioxolane | 76 | 69.9 | 0.596 | 1.059 | 32.55 | 3.04 |
| 2-methyltetrahydrofuran (MeTHF) | 80.3 | 100.9 | 0.475 | 0.849 | 24.68 | 3.77 |




## ❑ Step 3 - "Green" dope formulation

__Case study__

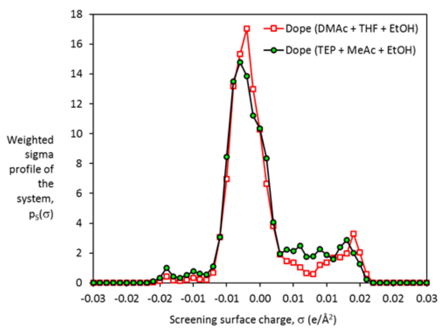
**Typical dope solution composition**

| Polysulfone dope solution (Magueijo et al, 2013) Component | % wt |
|---|---|
| Polysulfone | 22 |
| DMAc | 32 |
| THF | 32 |
| Ethanol | 14 |

**Potential substitution**

DMAc → TEP
THF → Methyl acetate

Approach based on:
- Conductor-like Screening Model for Real solvents (COSMO-RS) and the variant COSMO – SAC
- Database of sigma profiles compiled by Liu and co-workers at Virginia Tech (Mullins et al., 2006)




Composite sigma profile for the system / dope is given by the weighted sum of the sigma profiles of the individual solvents (Klamt and Eckert, 2000)

Novel dope composition is obtained by minimizing the differences between the original and the "new" weighted sigma profiles

| Example of "green" dope solution Component | wt % |
|---|---|
| Polysulfone | 22 |
| TEP | 39.7 |
| Methyl Acetate | 8.1 |
| Ethanol | 30.1 |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