

Six keys to green

Steve Pekarck and Joe Valcho of Novolyte Technologies look at how solvent choice can make the difference in a product's or a process's green credentials

You and your company are no doubt bringing new products to the marketplace and reformulating current products to meet more stringent regulatory and performance hurdles. Most chemical processes require the use of solvents and many chemicals are marketed as solutions or formulations in solvents. In many formulations, the solvent is needed for compatibility and contributes greatly to performance. The wise choice of a greener solvent can reduce commercialisation hurdles and speed product acceptance.

This article will provide a guide for the six keys to solvent choice. Finding a solvent that meets these six keys will improve time to market and profitability. The keys themselves are rather familiar, but using them together while choosing from less familiar solvents may be a new practice.

Solvent types span almost the entire range of organic chemical types, including hydrocarbons, halocarbons and oxygen-containing ethers, esters, alcohols and ketones. The physical properties of solvents include boiling point, partition factors, dielectric constant and Hansen parameters. Physical and performance properties can be put into six categories for consideration in solvent selection:

1. Solvent strength - to maximise concentration and temperature tolerance
2. Boiling point or evaporation rate - to develop a safe reaction process, with recycle or for a high performance formulation
3. Water solubility or insolubility - for separation efficiency
4. Stability in the presence of aggressive reactants - for recycle
5. Safety in handling - to minimise production and use hazards
6. Toxicological profile - for regulatory requirements and the market advantage of being 'green'

The choice of safer solvents is number eight of the famous Twelve Principles of Green Chemistry devised

by Anastas and Warner; incidentally a Google search under these principles yields some 381,000 hits, many with real-work examples from the chemicals industry.¹ However, as Table 1 shows, the right solvent can help to achieve the other principles to varying degrees.

As a matter of course, chemists, formulators and engineers design products and processes to maximise performance, while minimising cost and risk. This article will show examples of where the choice of solvent has met those goals, including following the 'Principles of Green'.

Factors for solvent selection

Figure 1 illustrates the key factors involved in solvent selection. The first factor to consider is the desired functions of the solvent. To dissolve or disperse is usually a given, but some solvents can provide additional performance (see below).

Secondly, how polar are the reactants or components of a formulation? If a reactant is involved, is it stable? Often we cannot use the principle of 'like dissolves like' for a reaction. Matching polarity while choosing a solvent type - say, aprotic - that will not participate in the reaction is necessary. The polarity match may be achieved using Hansen Parameters and dielectric constant.

We used the term 'solvent strength' to convey efficiency at dissolving or suspending reactants or formulation components. This may or may not be due to surfactant properties, which often overlap with solvent properties. However, glycol diethers and acetals do not have the polar and non-polar ends normally associated with surfactants, though they similarly reduce surface tension and aid wetting.

Once one or more solvent classes are chosen, based on polarity and function, a formulator can select a particular solvent that matches the desired boiling point range (based on assumed reaction conditions or desired evaporation rate) for an ink, adhesive, or coating. This part of the process is

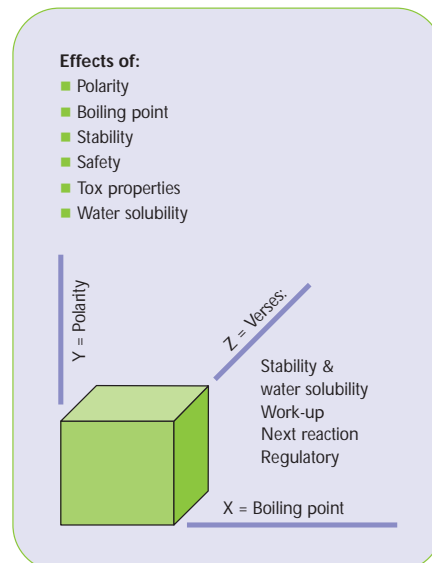


Figure 1 - Factors to consider in solvent choice

usually a good time to decide on water solubility and use this as a factor to choose between solvents.

Polarity and structure will determine both water solubility and stability to conditions or reactants. Experience, a review of relevant literature, and teamwork all help. Finally, regulatory concerns can be addressed. The internet is a great way to gather regulatory and associated process and formulation information.

When selecting a solvent in today's competitive world, cost is always a consideration. A new process or formulation should be two steps ahead of the competition to make the cost and effort of commercialisation worthwhile, so spending time on the selection process is well worth the effort.

The selection process described above has led coatings formulators to choose dipropylene glycol dimethyl ether (Proglyme) for its high solvency and moderate water solubility, leading to high performance with a minimal contribution to VOCs. The moderate evaporation makes it a suitable tailing and coalescence solvent.

Examples in practice

Seven factors are shown in Table 2 comparing Proglyme with two alternative solvents for coatings, texanol and tri-fluoromethyl-para-chlorobenzene (PCBTF). Proglyme is not a Hazardous Air Pollutant (HAP) and, as a propylene-based or P-series glycol, has an excellent toxicological profile. Odour is low compared to that of ester-alcohol texanol. Solvency for polar resins is higher than for PCBTF.

The higher glymes in Table 3 are non-HAPs and non-VOCs in Europe, and have excellent toxicity profiles. Their strong solvency makes them strong

Table 1 - Solvent choice & the 12 Principles of Green Chemistry

1	Prevent waste	Yes -	Increase yield and recycle
2	Design safer chemicals and products	Yes	
3	Design less hazardous chemical syntheses	Yes	
4	Use renewable feedstocks	As available	
5	Use catalysts, not stoichiometric reagents	Yes	
6	Avoid chemical derivatives	Yes	
7	Maximise atom economy	Yes	
8	Use safer solvents & reaction conditions	Yes	
9	Increase energy efficiency	Yes	
10	Design chemicals & products to degrade after use	Often	
11	Analyse in real time to prevent pollution	Yes	
12	Minimise the potential for accidents	Yes	

candidates not only for process solvents but also for cleaning, acid-gas scrubbing and formulating inks and adhesives.²

Higlyme is a chemically stable, aprotic and very strong emulsifier. Its six ethylene oxide groups, together with one methyl and one C₁₀ alkyl groups, give a water-soluble molecule that will try to bring organics and some inorganics into an aqueous emulsion. It is a strong cleaning solvent for speciality applications.

Higlyme can be a doubly green choice. For instance, a Novolyte customer was looking to commercialise a performance chemical for a functional fluid emulsion. Lab process development was being carried out in THF, but the manufacturing group asked if a safer alternative could be tested.

The customer's development group was also looking for an environmentally friendly (and compliant) emulsifier for the chemical and other additives, with the goal of maximising water and minimising cost. They added that an emulsion with high brine tolerance would be a definite plus.

We suggested that higlyme be used in place of THF, to stay in the product in order to serve as the emulsifier and also provide a level of brine tolerance. It actually delivered more performance than was requested.

Using 1,3-dioxolane (DXL), a polyester label may be applied to beverage or food containers without the use of an adhesive. Instead, a thin film of DXL is applied at the edge, then the film edges are overlapped slightly and squeezed together. As a powerful aprotic solvent, the DXL quickly disrupts the polymer chains and a bond is formed when these intersperse.

DXL has replaced both N-methyl-2-pyrrolidone (NMP), which is a substance of concern in the EU, and THF for newer seaming applications, such as with high-shrink wraps for wide bottles with narrow necks. Here the label actually shrinks over the cap, doubling as a security barrier.

DXL is also used to apply and remove photoresists, due to its ability to dissolve polar resins and its excellent toxicological properties. A second popular and bio-based acetal is glycerol formal (4-hydroxymethyl-1,3-dioxolane and isomer). This takes advantage of the diether dioxolane portion to increase the solvency of a glycerol-based alcohol.

Often, however, our customers have found it very green to go beyond 'like dissolves like' and replace objectionable solvents with glycol diethers for

Table 3 - Aprotic solvents that are non-VOCs in Europe

Non-VOC diether	Boiling point (°C)	Applications in addition to coatings as reaction solvents	% in water	Wt.% VOC (EPA Mehd 24 Run on Neat Additive)
Butyl diglyme	256	Inks, adhesives	0.3	100
Tetraglyme	275	Electronic cleaning, agriculture	100	12
Polyglyme	>300	Inks, acid-gas scrubbing	100	6
Higlyme	>300	Inks, cleaning, humectant for adhesives	100	6

demanding applications. These solvents often increase process safety while giving higher yield and less waste.

For example, monoglyme and diglyme (which are teratogen suspects) and 1,4-dioxane (a suspected carcinogen) are only provided for use in closed-loop applications with good engineering controls. These products are not to be used in so-called emissive applications, where either the industrial users or the consumer may be exposed to the solvents or vapours.

We describe these solvents as less green for two reasons. First, all glycol diethers are of low toxicity. Second, they can each be used in processes with aggressive reactants, where they increase yields and safety. They are also chosen because they reduce purification-derived waste, and can easily be recycled often many times because of their stability.

So 11 of the 12 principles of green are met. Safety and yield are increased and waste is decreased. And, when a biologically active API or drug is made, engineering controls will of necessity be in place to prevent worker exposure, as shown by the following two reactions.

Controlling exposure

Sodium borohydride (NaBH₄) has cost, safety and selectivity benefits over lithium aluminum hydride, due to its lower reactivity. The benefits of NaBH₄ are realised through the use of higher boiling glycol diether, in which the NaBH₄ is 50 times more soluble than in THF or diethylether.³

At room temperature, NaBH₄ is not capable of reducing esters. It does so readily at elevated temperatures, but protic solvents cannot then be used because the NaBH₄ would swiftly decompose. The use of tri- or tetraglyme for large-scale applications is recommended because of their better toxicological

and solubility profile.⁴ For example, an ester reduction at 162°C in diglyme eliminates the need for LiAlH₄.

This example and the one below take advantage of the amphiphilic behavior of glymes - that is, their ability to dissolve both polar and non-polar molecules. Glymes have a particular affinity for metal cations, due to their -O-(C-C)_x-O- structure, improving reactions for Grignards and other organometallics.

A second use of diglyme resulted in a patented, much greener process for one pharmaceuticals company. In their first patent, the discovery of an effective drug for the treatment of HIV was quite a triumph. In the second, the use of diglyme brought the health benefits of Neviripine to the world in a safer process, with higher yield and less waste, because:⁵

- The cation complexing properties of diglyme allowed the use of calcium oxide to neutralize hydrochloric acid liberated during a crucial amination step.
- The use of CaO allowed the use of less excess volatile amine
- Lower amine decreased the 435 psi reaction pressure to 90 psi
- Lower pressure increased safety while reducing required capital
- The yield increased from 74% to 90%
- The purification was simplified-again, using diglyme
- The diglyme is recycled, further reducing waste

The synthesis and purification was able to operate at the intersection of 'green'. That is a case in which a less green solvent increased safety and yield, decreased waste and is recycled. We view the point at which a solvent combines the right boiling point, polarity and toxicological profile as the green intersection of solvent optimisation.

References:

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Table 2 - Comparison of glymes with texanol & PCBTF

	Novolyte Higlyme	Novolyte Proglyme	Novolyte Glycerol Formal	Texanol	PCBTF
Chemical Description	Glycol diether	P-series Glycol diether	Bio-based Alcohol diether	Ester-alcohol	Halogenated Aromatic
Coalescent?	Yes	Yes	Yes	Yes	No
Odour	Mild	Mild	Mild	Ester	No
	Ethereal	Ethereal	Ethereal		
VOC exempt?	6% VOC	No	No	No	Yes in N. America
Rel Evap rate nBuAc=1	<0.01	0.13	0.04	0.002	0.9
BP °C	>300	175	192	254	139
Density	0.975	0.90	1.20	0.95	1.34
% in H ₂ O	100	35	100	0.1	0
%H ₂ O in	100	4.5	100	3.0	0